The Identification of Flat Glasses for Forensic Purposes

by

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SUMMARY

The many aspects of the Examination of Glass for Forensic purposes are studied. Refractive index and density are shown to be useful in distinguishing glass samples. The density of small fragments is determined using the sink/float method and the density of larger pieces by using Archimedes method. The refractive index of small fragments is determined using the Becke line technique and either the Reichert or Mettler hot-stages, with silicone fluid as the immersion liquid. Standard deviations as low as 0.00002 are recorded for refractive index using the Mettler hot-stage and silicone oil. The refractive index of larger pieces of glass and survey samples is determined using an Abbe refractometer.

The variation in both density and refractive index is measured across sheets of modern glass and it is shown to be necessary to take this variation into account when comparing samples. A number of surveys of glass samples are examined and their application to forensic science problems discussed. A statistical treatment of both refractive index and density is described to enable the similarity and discrimination to be assessed. The correlation between refractive index and density is also studied and taken into account.

A number of mathematical techniques for the objective interpretation of mass spectrometry photoplates are studied and it is shown that the Hull equation produces the most precise results yielding an average coefficient of variation of about 10% for 10 elements. Mass spectrometry is shown to be useful in distinguishing between glasses with similar major compositions,

but different trace element compositions and between glasses with the same refractive index and density. A trial shows that it is possible by using mass spectrometry to obtain an increase in discrimination of up to 20X over the discrimination obtained using physical properties.

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PREFACE

The work described in this thesis was carried out at the Home Office Central Research Establishment for Forensic Science at Aldermaston. At this establishment there is a long term project to investigate all types of glass which are likely to be encountered by the Forensic Scientist. This study represents the early stages of the project and is concerned with flat glass only.

The author was a member of a team led by Dr. E. F. Pearson (external supervisor) investigating the examination of glass for Forensic purposes. All the operations described in Part I of this thesis have been carried out by the author, but much of the repetitive routine work, notably in Section 6, was carried out by a Scientific Assistant using techniques and methods of approach developed by the author. The method described in Section 6.3 was first suggested by Dr. A. S. Curry.

Similarly in Part II all the operations described have been carried out by the author, but with practically all the samples studied, the processes up to the plate reading stage were carried out by the staff in the Mass Spectrometry Section.

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1. GENERAL INTRODUCTION

Forensic science is defined as the science used in courts of law. Forensic scientists are confronted with a number of rather particular problems, one of these being the small size of samples. The amount of material available may be only a single hair or fibre, a drop of blood, a few microgrammes of a drug extracted from body tissue or a milligramme of glass. In addition, it is generally necessary to examine and compare the sample and control specimens. The control consists of material of known origin such as a hair from the head of a person suspected of a crime, blood from the victim of an assault or glass from a broken window. Generally adequate amounts of control are available for analysis and there is no necessity to rely on micro-techniques. The 'sample' is examined to discover whether it is similar to the control and may consist of a single hair found at the scene of a crime, a blood spot on the clothing of someone suspected of inflicting an assault or a fragment of glass on the clothing of someone suspected of breaking and entering. In this case there is probably a very limited amount of material on which to carry out tests and micro methods of analysis must often be used.

In the comparison of the control and sample it is obvious that the same method of analysis must be used in each case. Therefore, the fact that there are relatively large amounts of control available may be of little value.

Having compared sample and control and decided that they are similar, it is then necessary to decide how the sample compares to the rest of the population from which it was drawn. For example, a certified report of a Ford motor car being seen

at the scene of a crime would not be very useful because there are millions of Ford cars in England. However, the presence of a yellow Lagonda at the scene of a crime would be regarded as good evidence because there are a strictly limited number of such cars. This problem of assessing the value of the evidence, the identification problem, is the more difficult of the two to solve because it necessitates adequate knowledge of the population from which the sample and control were drawn.

In the comparison of the control and sample a decision must be made as to whether they are similar or not. With discrete data such as blood groups, the problem is relatively simple (for example, fresh human blood is either rhesus positive or rhesus negative and cannot be in between). With continuous data such as refractive index, density, concentration, etc., the decision is rather more difficult in that exactly the same analytical result is not always obtained for both sample and control. How close the results from the sample and control are depends on a number of factors and this aspect is discussed more fully later in this thesis. The important point is that both the comparison and the estimate of the probability of occurrence should, as far as is possible, be based on sound mathematical tests rather than inspired guesswork. Such a procedure will largely eliminate any subjective assessment of the analytical results by the forensic scientist involved and, moreover, the evidence offered in court will be absolutely impartial. Such a procedure can only be applied to continuous data. However, fingerprints, shoeprints, etc. which require subjective assessment can still yield excellent evidence.

There are many types of glass that may need to be examined for forensic purposes. The most common types are window glass and container glass, but headlamps, windscreens and glass bulbs are submitted to Forensic Science laboratories for examination. Window glass presents difficulties because modern methods of continuous tank production yield a product that is remarkably constant in composition especially as regards major constituents. In addition, refractive index and density are often used for quality control purposes in the production of glass. These same two parameters are also used by the forensic scientist in the examination of glass. Because of its importance in forensic science, the work described in this thesis is solely concerned with the examination of window glass.

The production of modern glass is so carefully controlled that it is necessary to try to find other parameters by which glass can be compared. Various parameters such as dispersion and hardness[3,31,37] have been examined, but workers have found these to be of little value. Spectrographic analysis has been used[36], but this technique will normally only detect changes in the major constituents and these may often be detected by changes in refractive index or density.

The most promising means of increasing the evidential value of glass fragments is by analysis of the trace elements. When this work was initiated there were only two methods likely to give the necessary sensitivity and precision and these were neutron activation analysis and spark source mass spectrometry. Neutron activation has been studied by Coleman et al[214,215] and spark source mass spectrometry is currently being studied at

the Home Office Central Research Establishment. Particular attention has been paid to establishing a suitable mathematical technique for the evaluation of mass spectrometry photoplates and the statistical comparison of the results. The object of this was to remove, as far as possible, any bias being injected into the results by the analyst. Many computer programmes for the evaluation of mass spectrometry photoplates have been published, but are of limited use to the forensic scientist who does not normally have access to large computer installations. However, the theory behind some of these programmes has been used to develop a computer programme capable of execution on a small desk computer.

The number of cases involving glass samples which are submitted to the Forensic Science Laboratories in England and Wales is in the order of 20 cases per week, but each case may involve the examination of many glass fragments. It would be impractical, both from the analytical and cost effectiveness aspects, to analyse all these samples by sophisticated analytical techniques irrespective of whether they have the same refractive index and density. Therefore, rapid routine screening methods using density and refractive index will still be vitally important. Techniques for the examination of glass using density and refractive index have, therefore, been studied extensively, together with methods for the statistical treatment of the results.

PART I.

PHYSICAL PROPERTIES.

2. INTRODUCTION.

Forensic Science has been in existence for thousands of years. An early worker in the field was Archimedes (287-212 B.C.) who used his famous principle to determine the purity of gold. 2,200 years later Forensic Scientists still find the same principle useful in distinguishing glass samples. The Forensic Science service was established by the Home Office in the 1930's at which time density and refractive index were useful in glass examination due to the wide variation in these two properties from glass to glass. These parameters are still useful, but because glass production has become more tightly controlled the discriminating power of techniques using these parameters has become less.

In a paper discussing the refractive index of glass Davis[1] stated that both refractive index and density must be measured for complete identity. He reports authors assigning errors of 0.001 to 0.005 for the Becke line[85] method which was the most common method in use. (The Becke line is fully described in section 4.1.2.a). Refined procedures using temperature control and monochromatic light gave accuracies of about 0.0001, but Davis did list 12 disadvantages of the Becke line method based on using 'mixed liquids'. His method utilized the Christiansen effect using white light and he observed the colour change in the glass as the refractive index of the liquid was altered by adding more of one of the liquids. The refractometer readings were accurate to 0.002 or less. Using sodium light he obtained a precision of 0.001 with nitrobenzene and xylene as the immersion liquids contained in a large cell. A constant temperature device was not employed. In a later

paper[2] Davis used monobromobenzene and temperature control to vary the refractive index of the liquid. He stated that samples varying by 0.001 in refractive index at the wavelength of sodium light (n_d)could be distinguished by using the Becke line technique and sodium light as the source of illumination. Davis reported a temperature difference between the disappearance and reappearance of the Becke line of 2°C. which agreed with the figure obtained by Rees[4]. Graber and Principe[3] measured the refractive index of glass by varying the temperature to alter the refractive index of the liquid and took readings at 3 wavelengths. The refractive index at 589mμ (sodium D line) and also the dispersion (n_f-n_c) was calculated. The use of dispersion staining to find the most appropriate Cargille liquid was recommended and they gave a detailed discussion on the subject. (Cargille liquids are liquids of accurately known refractive index produced by the R. P. Cargille Laboratories Inc., Cedar Grove, N.J., U.S.A.) Graber and Principe discuss McCrones[83] discrimination index used to assess the value of a method in distinguishing between glass samples. The discrimination index is defined as:-

$$\text{Discrimination index (D. I.)} = \frac{\text{range of possible values}}{\text{range of experimental error}}$$

They stated that 90% of commercial optical glasses lie in the refractive index range 1.50 - 1.70 and that the temperature of the immersion fluid could be determined to ± 1.0 °C. Using Cargille liquids as the immersion fluid this was equivalent to a range of experimental error of 0.0008. Therefore

$$\text{D. I.} = \frac{0.2000}{0.0008} = 250$$

The dispersion of the same group of glasses ranged from about 0.007 to 0.023 and the measurement error was ± 2.0 °C. This gave

$$\text{D. I.} = \frac{0.016}{0.0016} = 10$$

The authors claimed that it is, therefore, possible to distinguish ≃ 2500 glasses between 1.5 and 1.7. The paper gave one example of two glasses which have the same refractive index at the wavelength of sodium light, but had different refractive indices at other wavelengths.

Rees[4] described a method which uses clove oil as the immersion liquid and a Köfler micro-melting point hot-stage to heat the sample. Three or four glass particles were mounted on the same slide in clove oil and viewed simultaneously in sodium light, but he suggested that green light should be used if a monochromator is available as the eye is more sensitive to light of that wavelength. The difference between the temperature of disappearance and reappearance of the Becke line was generally about 2°C. and he made two readings with the temperature increasing and two readings with the temperature decreasing for precise work. The refractive index was determined from a calibration graph. An alternative microscope micro hot-stage has been described by Peek.[67]

There are various other useful papers from sources outside the field of Forensic Science which describe methods for the determination of refractive index. Manners and Partridge[5] in a paper on the use of refractive index in quality control used a Bellingham and Stanley refractometer to measure refractive index to 4 places while Stephens and Rodney[65] used a high precision

spectrometer to measure to 0.00001. A paper by Hafner and Rood[6] considered some of the precautions necessary for precision measurements of refractive index and showed that they have reduced random errors to 2 in the 6th place with a Wild refractometer. Lists of stable monochromatic sources were also given, but the work was confined to optical glasses.

In a paper on the identification of synthetic fibres, Heyn[7] described the difference between the phenomenon of central illumination and Becke Line. The former was mainly the result of the refraction of light by the fibre and the latter was the result of the reflection of light at the interface of the fibre and liquid. In practice a composite effect was obtained. Faust[8] stated that the current explanation of the Becke line was that it was due to refraction and internal reflection of light at the specimen edge. A sample with an edge parallel to the beam of light gave a diffraction pattern (Becke line) on each side of the specimen edge and it was not possible to determine whether the liquid or solid had the higher refractive index. However, a sample with a tapering edge gave an asymmetric diffraction pattern and if the microscope objective was raised then the bright band moved towards the medium of higher refractive index. In contrast to Heyn[7], Faust[9] did not differentiate between the central illumination and the Becke line techniques. Faust measured refractive index by the method of mixing liquids. In a later paper[9], Faust further discussed the central illumination technique and discussed the mathematics of the method.

Various other workers have described instruments for the precise determination of refractive index. Johnson, Campanile

and Lefebre[10] described a refractometer for measuring differences in the refractive index of liquids to 1 x 10^{-6}. The instrument required 35µl of liquid and the sample cell was in the shape of a triangular prism. Hughes[63] described a refractometer accurate to 1 in the 5th place and Holmes[64] described a direct reading instrument accurate to 1 in the 4th place. Both of these instruments used a solid sample in the form of a prism.

An interesting paper by McCutchen[11] described a refractometer microscope which was used for both the microscopic examination of an object and for the measurement of its refractive index. The instrument was based on an Amici sphere (a glass sphere with a flat surface polished on it). In this method the sample for examination, which must have at least one flat surface, was brought into close contact with the flat side of the sphere. Incident light was passed through the Amici sphere to the sample which reflected the light back through the sphere and the following optical system. Refractive index was determined by adjustment of a pre-calibrated patch stop until the light field was just extinguished. The instrument described was an experimental prototype and could measure refractive index with a precision of $\pm$ 0.005. However, if a more accurately circular stop which was more precisely centred had been used then the authors claimed that the precision should be greatly improved. McAlister, Villa and Salzberg[12] measured the refractive index of glass in the infra-red using a Perkin - Elmer Model 12-C spectrometer. However, large samples were used and precision appeared to be in the 4th place. Pfund[13] also described a method for measuring the refractive index of solids, but the sample had to be polished and the method was only accurate to the 3rd place. For 'bulk'

refractive indices the sample was freshly ground and polished to remove surface films. Tilton, Rosberry and Badger[66] used an interferometer to measure the refractive uniformity of borosilicate glass after different annealing treatments.

Lauer and King[14] used two precision refractometers to measure the refractive index of organic liquids above ambient temperatures. Precautions were taken to ensure that no thermal gradients existed because of enlarged windows in the cell. The method used was based on that of Eykman[15] which involved rotation of the prism table rather than the telescope. However, Lauer and King point out that neither of these instruments is suitable for routine use. For n-hexadecane, trans-decahydronaphthalene and 1-methylnaphthalene they found a straight line relationship between refractive index and temperature over the range 75°C - 100°C. The densities of these organic liquids were determined using a 5ml Lipkin bicapillary pyknometer over a temperature range of 25 - 100°C. The density values were estimated to be accurate to two or three figures in the fourth decimal place. Lauer and King determined the refractive index using the same equipment as above and was thought by the authors to be accurate to $\pm$ 0.00005. The data was used in the Eykmann function which states that:-

$$C = \frac{n^2 - 1}{d(n + 0.4)}$$

where C = a constant

n = refractive index

d = density

It was shown that this equation accurately represented the relationship between refractive index and density for the liquids

examined.

Few papers have been written dealing solely with density and its application to Forensic Science and those that have, tend to favour density gradients for the comparison of glass fragments.

Greene and Burd[75] described a thermal density gradient which was established by heating both ends of a vertical tube of liquid using water circulated from two constant temperature baths. They reported that when using a mixture of bromoform and bromobenzene 500mg and 2.5mg samples of the same glass floated at different levels, but when an aqueous solution of potassium mercuri-iodide was used this anomolous behaviour was eliminated. The most sensitive gradient that was reported was 0.0006 $g\ ml^{-1}\ inch^{-1}$ using potassium mercuri-iodide as the liquid in which the glass samples were suspended. This allowed density differences of 0.00006 $g\ ml^{-1}$ to be observed. McCrone and Hudson[76] have reported a density column formed by mixing any two of a number of organic liquids and the authors stated that two glasses floating at the same level had the same density to within at least $\pm$ 0.0005 (no units given). The paper also described an experimental method for examining geological material using aqueous thallium formate-malonate as the liquid in which the samples were suspended.

Kind and Summerscales[77] described a simple apparatus for establishing a density gradient. It consisted of a 10ml measuring cylinder containing a suitable liquid which was heated from above by an Anglepoise lamp. A thermal gradient was readily established which could be calibrated by the method described by

the authors.

An important paper by Knight[16] described a method for the determination of glass densities which was reported[17,21] to be widely used. The apparatus consisted of a shielded glass water bath containing heater coils and a stirrer. Five test tubes were suspended in the water, each containing a mixture of α-bromonaphthalene and s-tetrabromoethane. The glass samples weighing about 2 grams were placed in these tubes, together with suitable calibrated standards. The temperature was raised at the rate of 0.1°C min^{-1} and the temperature noted at which the samples sank past a line inscribed on the sides of the test tubes. The standard deviation of this method was quoted as 0.0001g cm^{-3}. The apparatus was also described in detail elsewhere[68]. In a paper primarily concerned with bottle glass Duff[69] used a method similar to that of Knight[16] to measure density variation with approximately the same precision. Ghering[73] discussed the statistical control of the density of glass during production and showed the range of probable values.

A paper by Primak and Day[18] considered the problem of measuring the density of small crystals weighing less than 1mg. The authors claimed the viscosity of the liquid, the size of the particle, the duration of the observation and the presence of foreign matter on the crystal were critical factors. The method described was a floatation method whereby repeat determinations were performed, washing between each determination until constant results were obtained. This ensured the removal of foreign matter but was laborious.

Johnson and Hutchinson[19] determined the electrolytic separation factor of lithium isotopes using a density technique.

A floatation medium of bromoform and small amounts of n-pentanol and n-hexanol as stabilizers was used. Floatations were performed in glass stoppered tubes in a water bath whose temperature was controlled to 0.001 ^{o}C (equivalent to 2.49×10^{-6} $g.ml.^{-1}$) and the floatation point was reached by adjusting the temperature so that the crystal was just rising and then readjusting until the particle just sank.

An ingenuous, but somewhat cumbersome apparatus was described by Haller and Callcamuggio[20] to measure extremely small weight, volume and density changes. The sample was held in a holder attached to a thin glass sphere. The float was immersed into water and its position adjusted by varying the air pressure above it.

Simons[22] used a floatation technique to determine the density of solids over a density range of 5 to 21g ml^{-1} and volume range 10^{-4} to 10^{-3} ml. He fixed the sample to a sheet of Mylar film to give a gross density of between 1.4 and 2.7g ml^{-1}. The gross density was then determined in the normal manner and the density of the sample determined by calculation. Simons' method was not as accurate as the falling velocity method of Roy[23] who claimed a relative error of 0.1%. However, it was more accurate than displacement methods. Taylor and Doyle[70] used a similar method to Simons to determine the density of titanium dioxide using thallous formate solution as the floatation medium.

Staton and Maycock[24] used both Archimedes method and the sink-float method to determine the density of solids and claimed an experimental error of around $\pm$ 0.0003g cm^{-3}. Sample size varied between 2g and 6g.

The density of solids may be determined by comparison with standards of known density in a density gradient column which has been prepared by the controlled mixing of two liquids of different densities. One paper[25] described the mass production of such gradients, but it has been reported[26] that there are difficulties in using them in routine Forensic work.

Kirk and Russel[29] described a method for the determination of the specific gravity of small glass fragments, but only claimed an accuracy in the third place of decimals.

Collett[71] discussed the simplification of calculations for the hydrostatic weighing method whilst still considering buoyancy and other corrections. In a later paper[72] he used the hydrostatic weighing method to determine the density of 5 optical glasses. Knight[74] described a method for dealing with temperature and air buoyancy corrections in the determination of the density of container glasses and Glazebrooke[100] has discussed the many corrections that may be applied to the various forms of density determination.

A publication by the United States Department of Commerce[52] described various methods for the determination of the densities of both solids and liquids and various A.S.T.M. and B.S. specifications exist for the determination of density. The Lipkin bicapillary pyknometer[27,28] offered an accurate way to determine the density of liquids and a reproducibility of 0.0002 was quoted in the first reference and 0.0006 in the second. A standard[34] published by the Standard Tar Products test committee described another method for the determination of the density of liquids using a capped pyknometer, but no expected accuracy was mentioned.

The Forensic examination of glass as currently practised generally includes the determination of both density and refractive index although both properties have been shown to be correlated[30]. Some workers[3,37] also examine other physical parameters such as colour, dispersion, etc.

A paper by Mullen[31] described a method for the determination of both refractive index and density of glass. Density was determined by Archimedes method with a standard deviation of 0.0011g cc^{-1}. The refractive index was determined by the Becke line method using a water heated hot stage and a standard deviation of 0.00013 was reported. Dispersion was not found useful in distinguishing glasses and in addition no variation across a pane was reported c.f.[32].

A paper by Tryhorn[33] reviewed the methods of glass examination. He showed how the point of impact on a piece of glass could be determined from the way in which it had fractured and described some simple ways by which the density and refractive index could be compared. He also suggested a way by which a rough estimate of the hardness of the glass could be made by their mutual scratching properties. Colour, ultra-violet fluorescence, chemical composition, thermal analysis, polish marks and "Griffith's cracks" were also briefly discussed.

Marris[35] stated that using mixed liquids he could determine refractive index to 0.002, but also claimed that specific gravity was a more discriminating test.

The use of density and refractive index in the examination of glass was discussed by Kimber and Waller[36]. They briefly described techniques available and stated that it was possible to distinguish between samples of glass differing by

0.002 in density and 0.001 in refractive index. Therefore, if the range of values for refractive index and density was 1.5100 - 1.5330 and 2.475 - 2.553 respectively, then there are 39 divisions in the density range and 23 in the refractive index range. They suggested that taking correlation into account the chance of selecting two glasses of the same density and refractive index was about 1 in 100. They also stated that fluorescence under ultra-violet light and hardness were of doubtful value and that spectrographic analysis was unhelpful due to the small sample size and the similarity between the glasses. Physical fit and types of breakages were also discussed.

Nelson[37] in a paper describing the examination of 50 Lucas 700 headlamp glasses reported a standard deviation of 0.001g cc^{-1} on his density determinations using a floatation method. The refractometer readings were subject to an error of 0.0001. Nelson also examined colour and hardness by a previously described method[33]. Each of the fifty samples could be distinguished from each other.

Gamble, Burd and Kirk[38] pointed out that Winchell[39] and Wright[40] had shown exact correlation between the composition of glass and its physical properties. They also used an immersion method to determine the refractive index to 0.0005 and claimed that by adding liquid dropwise they were able to detect differences in samples mounted together of less than 0.00005. The specific gravity was measured as described by Kirk and Russel[29]. All 100 glasses examined from different sources were found to be different and they found no proportionality between refractive index and density differences in any instance. In addition, they found that all glasses could be distinguished by

refractive index alone, but that some of the differences may have been due to manufacturing imperfections. Specific gravity was not found as useful. Some causes of heterogeneity were also suggested and they reported that they found minute variations in windows and large bottles.

MacDonell[41] pointed out the usefulness of spectrochemical analysis. He suggested that density, refractive index and coefficient of thermal expansion would all be useful to the forensic scientist. This paper is primarily intended to identify the <u>type</u> of glass and the values of each physical property shown cover a large range of values. Density was determined by Archimedes method, the sink-float method or by indirect use of a pyknometer, and refractive index by the Becke line method or by using an Abbe refractometer. The coefficient of thermal expansion was measured on a pointed glass rod 4" in length or by the composite fibre method. However, he did not explain how this measurement could be made on samples of the size encountered by the Forensic scientist.

Bastick and Gould[42] pointed out that although density had been very popular for the quality control of glass there were a number of objections to the choice of density. They emphasized that Ghering[43] had already listed three reasons for the choice of density, but that they also considered some of the difficulties. Bastick and Gould stated that difficulties in the measurement of density were mentioned in several papers[16,44,45], and these workers favour the use of the reflex prism refractometer described in detail by Holmes[46], but this instrument only gives a comparative reading.

Bastick and Gould[42] also considered the variations of refractive index and density with composition and this aspect was further examined in a theoretical paper by Isard[47] who showed that physical tests could be used to describe the composition of glass, (n - 1) tests being necessary for an n component glass. He also described how variations in physical properties were a measure of the change in composition, but did not give any details of experimental procedure for the determination of density and refractive index. However, Isard did state that because of the relationship between density and refractive index, only one of them should be chosen. Dabbs and Pearson[30] have shown that there is a high correlation between these two properties. Other workers[48,49,50] have discussed the relationship between physical properties and composition and also the relationship between refractive index and density, but have given no experimental details for either parameter. A paper by Ritland[79] showed that for borosilicate crown optical glasses that have been subjected to different thermal histories, the Lorentz-Lorenz equation did not hold and that the Drude equation provided a more accurate description of the relationship. However, Ritland did show a high degree of correlation between the density and refractive index for this single borosilicate glass.

A report by the Physical Properties committee of the Society of Glass Technology[51] described experiments in which prepared samples of optical glass were sent to various laboratories for the determination of density and refractive index. It was reported that taking all the results from all the laboratories into account, a standard deviation of 0.0005 was obtained for density using Archimedes method on samples exhibit-

ing a density of 2.5g cc^{-1}. Using the V-block method for the measurement of the refractive index of the glass samples, a standard deviation of 0.0001 was obtained in between-laboratory experiments. A value of between 0.0001 and 0.0002 was obtained in a similar series of experiments using an Abbe refractometer. In the majority of cases air buoyancy corrections were applied to the density and the weight of the supporting wire was taken into account.

Heterogeneity is of interest to the Glass Technologist in that its presence in flat glass is liable to make it commercially unacceptable. The Forensic Scientist is interested in heterogeneity because any variation across an area of glass under consideration will need to be accounted for in comparing the control sample with the crime sample.

Budd and Blanchard[53] used a modified Shelyubskii[54] technique to determine the micro-inhomogeneity in glass from the measurement of the refractive index distribution. They used 2.5g samples of crushed glass with a mean particle size of 60 microns which were placed in photometer cells with 2.5ml of chlorobenzene. The cells were placed, in turn, in a water jacketed cell mount and the spectral absorbance determined at different temperatures. Using their double wavelength method they found a standard deviation of 0.002 in terms of refractive index and this was found to increase only slightly as the particle size was reduced. The mixing of two different glasses yielded an increase in standard deviation showing that gross inhomogeneity could be detected. Again using the Shelyubskii method, Schilling and Weiss[78] measured the heterogeneity of several glasses. They found the heterogeneity in flat glass to be 0.000276 in terms of

standard deviation which is in good agreement with the value obtained by Dabbs and Pearson[32]. In addition the authors showed that heterogeneity did not increase as the particle size decreased in agreement with the work carried out by Budd and Blanchard[53].

On a somewhat larger scale Cable and Bower[55] examined the homogeneity of 50g laboratory glass melts using Shelyubskii's light scattering method[54] and Löffler's[56] etching and interferometry technique.

A paper by the Physical Properties Committee of the Society for Glass Technology[57] discussed terms used to describe heterogeneity and techniques for assessing it. Methods were discussed for the examination of both micro and macro heterogeneity usually by examining the optical effects caused by the heterogeneity.

Little work has been published on the distribution of density and refractive index of glasses, but two papers[31,80] describe small collections (under 200 samples in each case) taken from cases arriving at Home Office Forensic Science Laboratories. Mullens paper[31] showed a bimodal distribution which contained a relatively large amount of glass of higher density than modern production glass. However, the paper by Cobb[80] showed much less glass in the high density peak.

Dabbs[81] described a method whereby the density of a large number of samples could be determined at the same time. The distributions of two glass populations obtained from non-criminal sources were given which were very similar to the distribution obtained by Mullen. The largest distribution described is that by Dabbs and Pearson[30] who have measured the refractive

index of 939 samples of glass collected from the scenes of fires. In addition, the density of 338 of these samples were determined by Archimedes method.

Various other workers[38,41] in the United States have studied small numbers of a wide range of glass samples obtained from various sources, but have not discussed the probability of occurrence of the more unusual glasses.

To estimate the frequency of occurrence of a glass with a given property it is necessary to know how this property varies throughout the population from which the glass has been drawn. As early as 1935 Tryhorn[59] discussed probability and circumstantial evidence, but did not give any suggested mathematical treatment of the subject. More recently, Nickolls[82] suggested some probabilities of selecting two identical glasses in different housing areas, but did not show how he calculated these probabilities. He also showed a graph of number of samples vs specific gravity for various glasses, but his data disagrees markedly with the distributions published by other workers[30,31,80,81]. A paper considering the basic principles concerning the use of statistics in Forensic Science has been written by Kingston and Kirk[58], but they described no actual statistical methods to deal with Forensic Science problems.

Probably the most useful published papers are by Parker[60,61] who describes a somewhat complicated technique specifically designed to deal with the neutron activation analysis of hair[62], but is equally applicable to other Forensic science problems including glass.

3. THE DETERMINATION OF DENSITY

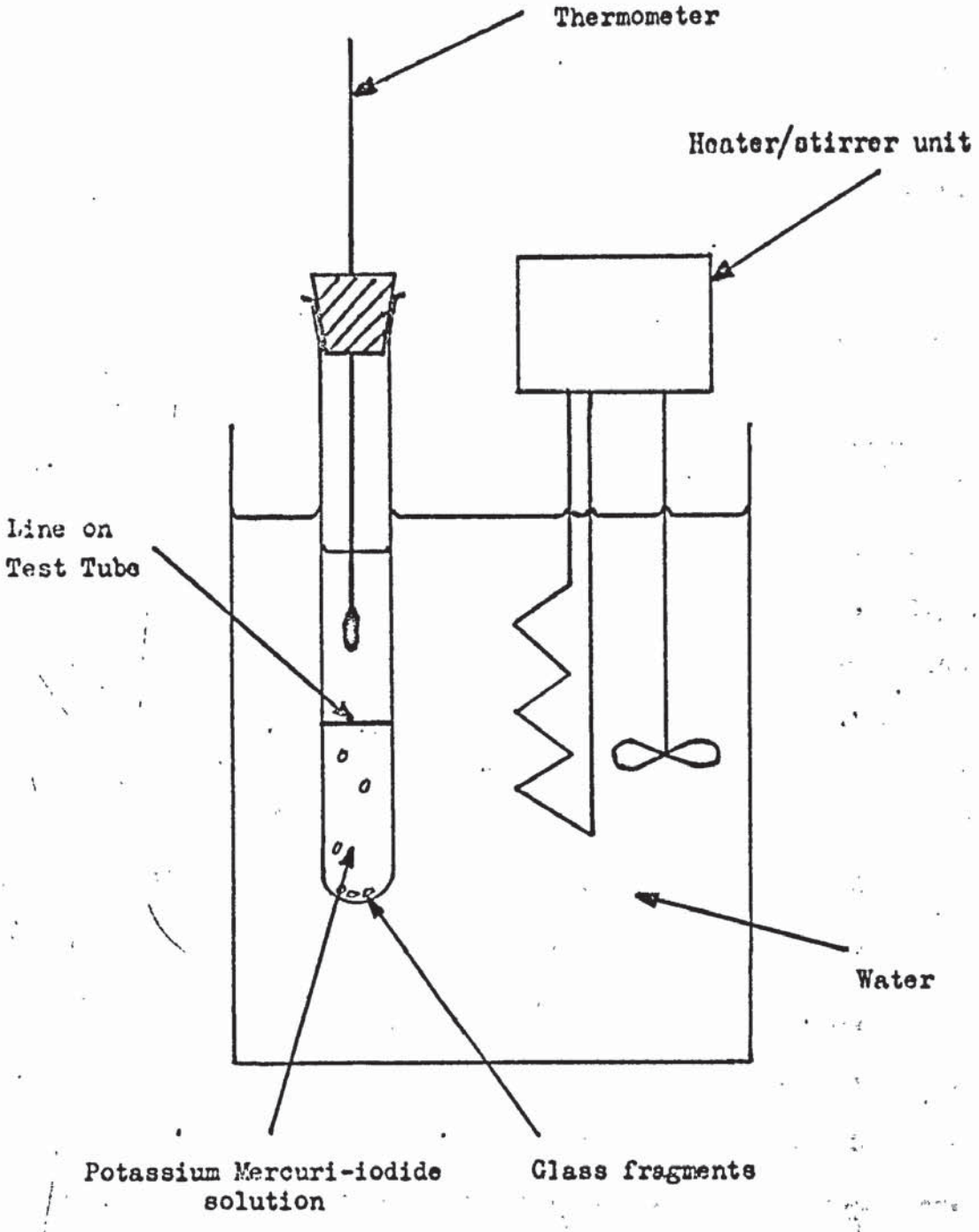
3.1 EXPERIMENTAL

3.1.1. Sink/float method

The apparatus used for the determination of density by the sink/float method is shown in Figure 1. A test tube measuring 300mm x 12mm was used for samples weighing up to 0.1g and a 300mm x 27mm test tube was used for larger samples.

The glass samples under examination, together with standard glasses whose densities were accurately known were placed in the test tube, together with a solution of aqueous potassium mercuri-iodide. The density of the liquid was adjusted by the addition of distilled water or saturated potassium mercuri-iodide solution until the most dense glass was just floating at room temperature. The test tube was placed in the water bath and the temperature raised from room temperature by means of the 'Tempunit' heater/circulator unit until all the glasses had sunk. The whole apparatus was then allowed to cool slowly causing the density of the liquid to increase. The temperature was noted at which each piece of glass passed the line inscribed on the wall of the test tube. The test tube was rotated once every three minutes to ensure that none of the glasses were sticking to the bottom. The known densities of the standards and the temperature at which they passed the line on the test tube was plotted on linear graph paper and the best straight line fitted through the points. The densities of the unknown samples were then read from this calibration graph. Some results for different glasses are shown in Table 1. The standard deviations found show the overall precision obtained in determining the density of the unknown.

FIG. 1



SCHEMATIC DIAGRAM OF THE APPARATUS USED FOR DENSITY DETERMINATION BY THE SINK/FLOAT METHOD.

TABLE 1

Determination of the precision of the sink/float method using B.G.I.R.A. standards. Replicate determinations on 6 fragments of glass

Glass	1	2	3	4	5	6
Density $g\ cm^{-3}$	2.4975	2.5186	2.5079	2.5040	2.5085	2.5096
	2.4978	2.5192	2.5070	2.5040	2.5089	2.5106
	2.4973	2.5194	2.5068	2.5045	2.5088	2.5108
	2.4982	2.5181	2.5073	2.5046	2.5085	2.5095
	2.4973	2.5189	2.5074	2.5041	2.5087	2.5102
Mean	2.4976	2.5188	2.5073	2.5042	2.5087	2.5101
Standard Deviation	0.0004	0.0005	0.0004	0.0003	0.0002	0.0006

If standards were not available, the difference in temperature at which the unknown glasses passed the mark on the wall of the test tube was measured and the density difference between the fragments calculated from the known temperature coefficent of the liquid (vide infra).

Two sets of standards were used, one being supplied by the British Glass Industries Research Association (B.G.I.R.A.) and the other by Pilkington Brothers. The latter were supplied as specific gravity standards, but on conversion to density using the equation

Density = specific gravity x density of water at the temperature at which the specific gravity was measured.

the agreement between the two sets of standards was to within 0.0025g cm^{-3}, the Pilkington samples being the less dense. The discrepancy was investigated by preparing standards covering a limited density range from glass that was available in the laboratory. The density of the glass was determined on pieces weighing over 20g using Archimedes method (see section 3.1.2.). A small fragment weighing approximately 0.5g was cut from each of the large pieces and these fragments are referred to as the C.R.E. standards. These standards were then compared with the other two sets of standards using the sink/float method. The known density of each standard was plotted against the temperature at which it passed the line and the best straight line fitted to each set of results using least squares. The results are shown in Figure 2.

The temperature coefficient of density of the potassium mercuri-iodide was calculated using the previously described technique with the standard samples obtained from the British Glass Industries Research Association. The standard samples were placed in the test tube with the potassium mercuri-iodide and the temperature recorded at which they rose past the line. Two solutions were used (A and B) with different concentrations of potassium mercuri-iodide covering the range 2.47 - 2.53g cm^{-3}. A plot of density vs temperature is given in Figure 3.

3.1.2. Archimedes method

The glass whose density was to be determined was cut to the required size to give a sample weight of 15g or over and cleaned in hot concentrated nitric acid followed by a wash in distilled water. The density was determined by weighing the glass in air and again in demineralized water using an Oertling constant load four place balance. There was no evidence that it was

necessary to use freshly boiled water (Table 2). No air buoyancy correction was made, but the weight of the suspending thread was taken into account in the calculation.

TABLE 2

The effect on the results of using boiled water in the determination of density by Archimedes method.

	BOILED WATER	DEIONISED WATER
	2.4817.	2.4819
	2.4818	2.4818
	2.4819	2.4814
	2.4815	2.4817
	2.4815	2.4814
	2.4820	2.4815
	2.4815	2.4816
	2.4814	2.4813
	2.4811	2.4812
	2.4810	2.4813
Mean	2.4815	2.4815
Std. Dev.	0.0003	0.0002

A series of experiments were performed to determine the minimum weight of glass that should be used and to determine the best type of supporting thread. After some preliminary experiments with several types of thread, five density determinations were made on a piece of modern sheet glass weighing approximately 60g using 0.1mm diameter tinned copper wire as the supporting

thread. Five further determinations were made using 0.1mm diameter nylon monofilament supporting thread (1.3 lb breaking strain nylon fishing line). About 10g of glass were then cut off and the two sets of determinations repeated on the remainder. This procedure was repeated until there was only about 1g of glass remaining and the results are tabulated in Table 3. The standard deviations are calculated from the range as described by Dixon and Dean[93].

Density may be calculated from the formula.

$$\text{Density} = \frac{\text{wt. of sample in air} \times \text{density of water}}{\left[\begin{array}{c}\text{wt. of spl. in}\\ \text{air}\end{array}\right] - \left[\begin{array}{c}\text{wt. of spl. +}\\ \text{thread in}\\ \text{water}\end{array}\right] - \left[\begin{array}{c}\text{wt. of thread}\\ \text{in water.}\end{array}\right]}$$

However, because the weight of thread was small and the effect of the surface tension of the liquid on the thread was relatively large, this resulted in a high degree of uncertainty for the term 'wt. of thread in water'. Therefore, this term was replaced by the 'wt. of thread in air', thus reducing the equation to

$$\text{Density} = \frac{\text{wt. of sample in air} \times \text{density of water.}}{\left[\begin{array}{c}\text{wt. of spl. +}\\ \text{thread in air}\end{array}\right] - \left[\begin{array}{c}\text{wt. of spl. +}\\ \text{thread in water}\end{array}\right]}$$

The results calculated by this equation are also shown in Table 3 under the heading of modified equation.

The long term precision of the method was estimated by making replicate determinations of the density on a 25g piece of glass over a period of 3-4 months. In all, 75 determinations were made and these yielded a standard deviation of 0.0003g cm^{-3}.

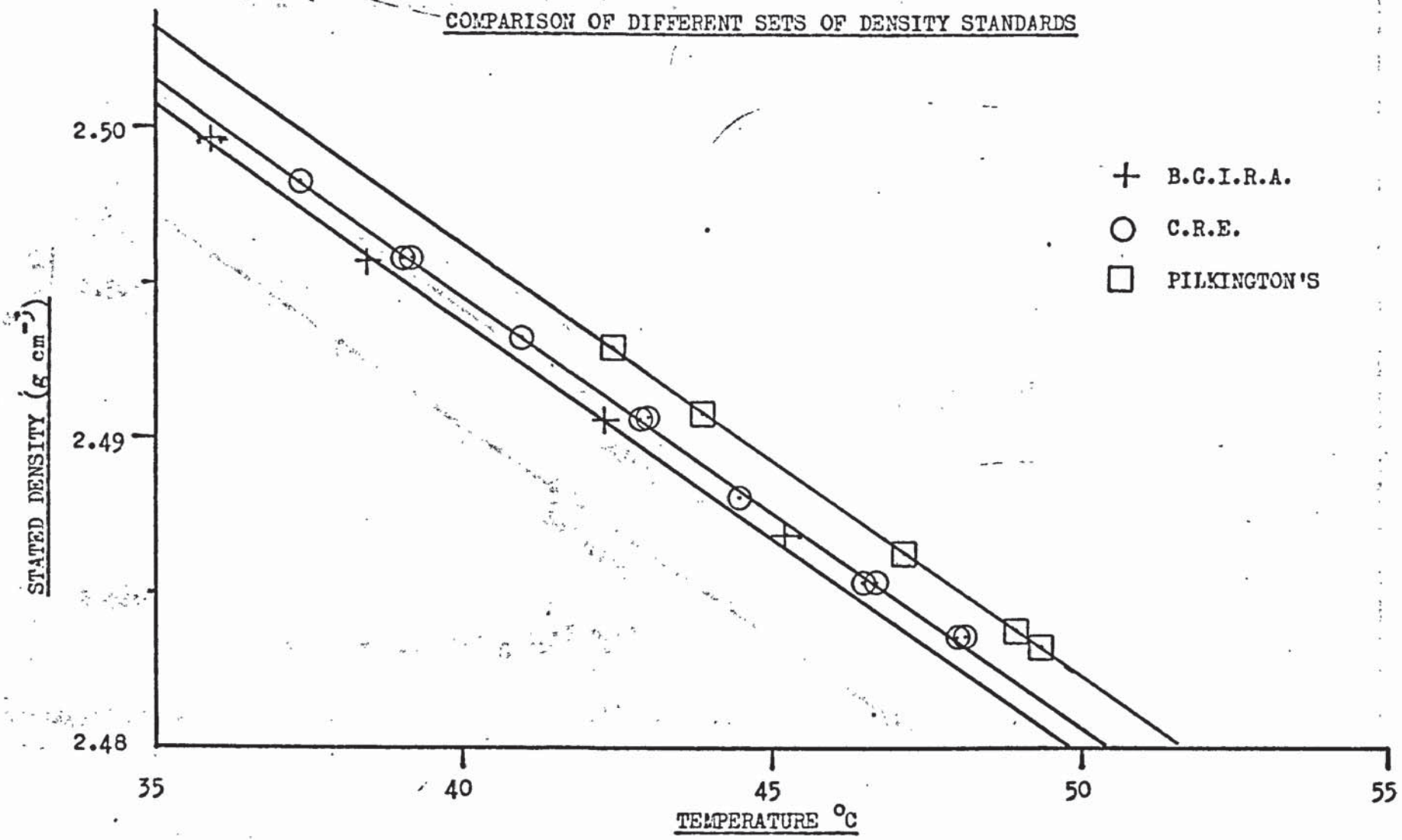

COMPARISON OF DIFFERENT SETS OF DENSITY STANDARDS
2.50
2.49
2.48
STATED DENSITY (g cm⁻³)
35
40
45
50
55
TEMPERATURE °C
B.C.I.R.A.
C.R.E.
PILKINGTON'S

FIG. 2

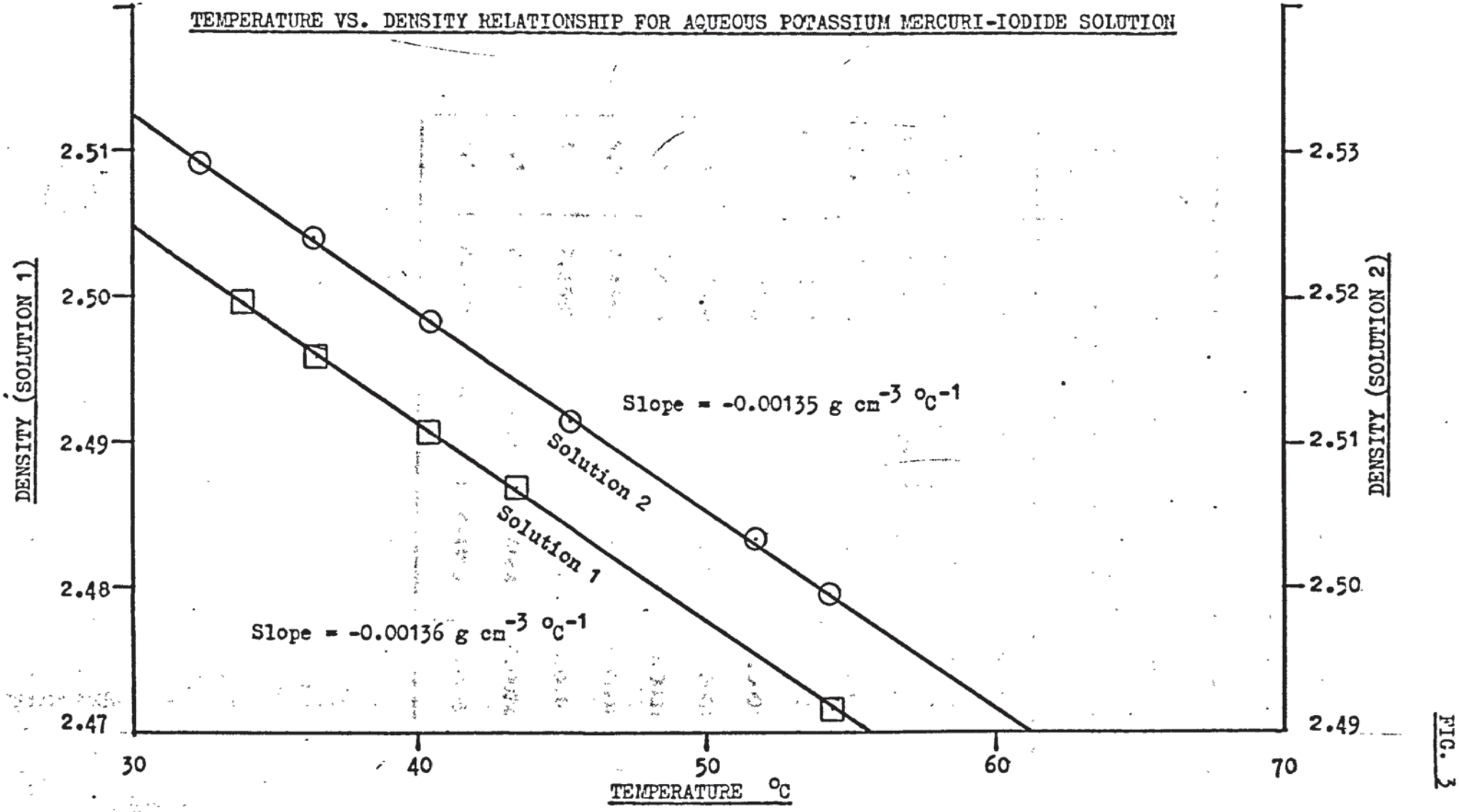

TEMPERATURE VS. DENSITY RELATIONSHIP FOR AQUEOUS POTASSIUM MERCURI-IODIDE SOLUTION
DENSITY (SOLUTION 1)
DENSITY (SOLUTION 2)
2.51
2.50
2.49
2.48
2.47
2.53
2.52
2.51
2.50
2.49
30
40
50
60
70
TEMPERATURE °C
Slope = -0.00135 g cm^{-3} °C^{-1}
Slope = -0.00136 g cm^{-3} °C^{-1}
Solution 2
Solution 1

FIG. 3

TABLE 3

Effect of the weight of the sample on the accuracy and precision in the determination of density by Archimedes method.

Wt. of sample (g)	Copper Wire			
	Normal equation		Modified equation	
	Density	S.D.	Density	S.D.
60.9	2.4857	0.0001	2.4855	0.00004
47.6	2.4857	0.00004	2.4855	0.00004
36.4	2.4857	0.0001	2.4855	0.00004
29.8	2.4858	0.0001	2.4857	0.00004
25.4	2.4857	0.0002	2.4855	0.0001
20.0	2.4854	0.0003	2.4855	0.0001
15.0	2.4850	0.0002	2.4848	0.0001
9.5	2.4853	0.0002	2.4856	0.0001
5.9	2.4855	0.0004	2.4855	0.0007
3.8	2.4852	0.0008	2.4852	0.0010
2.1	2.4846	0.0023	2.4864	0.0024
1.1	2.4825	0.0026	2.4855	0.0015

TABLE 3 (Cont'd.)

Wt. of sample (g)	Nylon Filament			
	Normal equation		Modified equation	
	Density	S.D.	Density	S.D.
60.9	2.4856	0.0001	2.4856	—
47.6	2.4856	0.00004	2.4855	—
36.4	2.4861	0.00004	2.4860	0.00004
29.8	2.4856	0.0001	2.4856	0.0001
25.4	2.4857	0.0003	2.4856	0.00004
20.0	2.4853	0.0002	2.4855	0.00004
15.0	2.4850	0.0002	2.4851	0.0001
9.5	2.4854	0.0002	2.4858	0.0002
5.9	2.4852	0.0006	2.4852	0.0001
3.8	2.4848	0.0008	2.4854	0.0006
2.1	2.4854	0.0009	2.4871	0.0010
1.1	2.4825	0.0044	2.4856	0.0018

3.2 DISCUSSION

The sink-float method gives reasonably good results although the standard deviations given in Table 1 are not as good as those quoted by Knight[16] who used a similar method. This is probably due to the fact that he used a rather better insulated apparatus than was available in this study, with better temperature control.

None of the three sets of standards agreed with each other. The C.R.E. standards lay between the two sets of standards obtained from outside sources. Figure 2 shows the stated density of each standard plotted against the temperature at which they sank past the line inscribed on the side of the test tube. Inspection shows that for any given density the Pilkington standards are less dense than the C.R.E. standards by 0.0017g cm^{-3}. The B.C.I.R.A. standards are denser than the C.R.E. standards by 0.0008g cm^{-3}. It therefore follows that, with respect to the C.R.E. samples, the values of density quoted for the Pilkington samples were too high and the values given for the B.C.I.R.A. samples were too low. It is not clear which set of standards are correct. However, this is not important as long as only comparative measurements are being made.

Any small differences in the standards will not effect the calculation of the temperature coefficient of density of the potassium mercuri-iodide as this is essentially a comparative measurement. Figure 3 shows that the value obtained with the B.C.I.R.A. standards is -0.00135g cm^{-3} $^{o}C^{-1}$ and agrees well with the value given by other workers[75].

The results obtained from the determination of density using Archimedes Principle are interesting. Table 3 shows the

average result obtained from 5 replicate determinations on various weights of glass as previously described. In addition, the standard deviation of the replicate determinations are shown as this is a convenient and generally accepted method for the measurement of dispersion in a set of experimental results. Considering the results in which copper wire was used as the supporting thread, it is seen that there is little difference in the values obtained for density if the weight of the sample is above about 4g. Below 4g the result obtained from the modified equation is nearer to the result obtained using large glass samples. In addition, for samples weighing over 6g the standard deviation is less using the modified equation.

Using a nylon monofilament gave results which were in good agreement with those obtained when using a copper wire. The use of the modified equation does not alter the value of the density, but tends to be more precise. Therefore, the best method is to use glass samples weighing at least 15g and a nylon monofilament. The density should be calculated using the modified equation.

When this method was used to prepare density standards, the results obtained did not agree with standards obtained elsewhere (vide supra). Obviously to produce density standards which were very accurate it would be necessary to use a 5 or 6 place balance and to take other variables into account such as air buoyancy and the effect of surface tension on the thread. This procedure would be tedious when large numbers of samples were involved such as when conducting a survey and the extra effort involved is not justified. In Forensic science it is not necessary to know the density of a piece of glass accurately, but

a precise method is required when comparing two glass fragments. In addition, when estimating the probability of occurrence of a glass fragment it is necessary to have a reproducible method that can easily be carried out by all operators. A reproducible but not necessarily accurate method allows the Forensic Scientist to compare the results obtained from the glass under examination with similar data obtained on many other glass samples. The method described above (section 3.1.2.) fulfils this requirement provided that the experimental method is closely followed.

4. THE DETERMINATION OF REFRACTIVE INDEX

4.1 EXPERIMENTAL

4.1.1. By Using an Abbe Refractometer

A Hilger and Watts Abbe refractometer was used to measure the refractive index of glass samples measuring 1cm square or more. The refractometer was initially standardized against the piece of glass supplied with the instrument and all values of refractive index quoted in this thesis are referred to this block of glass.

The samples were cut to a suitable size to ensure good contact with the prism, but the edges were not polished. Eight readings were taken on each sample, one on each edge on each face using one spot of 1-bromonapthalene as a contact liquid between the sample and the prism. All refractive indices reported in this thesis were measured using sodium light. The results are shown in Table 4.

TABLE 4

Replicate readings taken on standard and reference sample on the Abbe refractometer.

	No. of results	Standard Deviation
Single reading on polished standard	50	0.00016
Single reading on one edge of rough cut sample	50	0.00012
On means of one face of rough cut sample	50	0.00008

4.1.2. By using the Becke line and a Reichert Hot-stage

(a) Reichert Hot-stage Apparatus. The Reichert hot-stage microscope is shown diagrammatically in Figure 4. It was originally designed by Koffler for the micro determination of melting points on very small quantities of organic solids. The apparatus consists of a solid metal plate with a hole drilled in the side to take the thermometer. Beneath the plate is the heating element held in place with a thin metal disc and a circlip. In addition, there is a hole drilled through all three components so that light may be transmitted through the heating assembly to a sample on a microscope slide placed on top of the metal block. The apparatus is mounted on a suitable microscope stage and the sample observed through the microscope. Current is supplied to the heater using a Variac control which must be carefully and frequently adjusted to obtain the correct heating rate. The original thermometer was graduated from 0-360°C in 1°C intervals and was designed for melting point determinations. To increase the sensitivity of the apparatus, this thermometer was replaced with one reading 20-100°C in 0.1°C intervals. It was found necessary to pack the thermometer cavity in the hot-stage with silicone grease (type MS4) to ensure good thermal contact. In addition, it was necessary to keep the heating rate at about 0.2-0.4°C min^{-1} as the temperature approached match point to ensure thermal equilibrium between the sample and thermometer. Controlled cooling was achieved by reducing the heater power to a suitable level.

A fragment of glass or about 1mg of crushed glass was placed in the centre of a single cavity microscope slide and two or three drops of the immersion liquid added. The cavity, sample

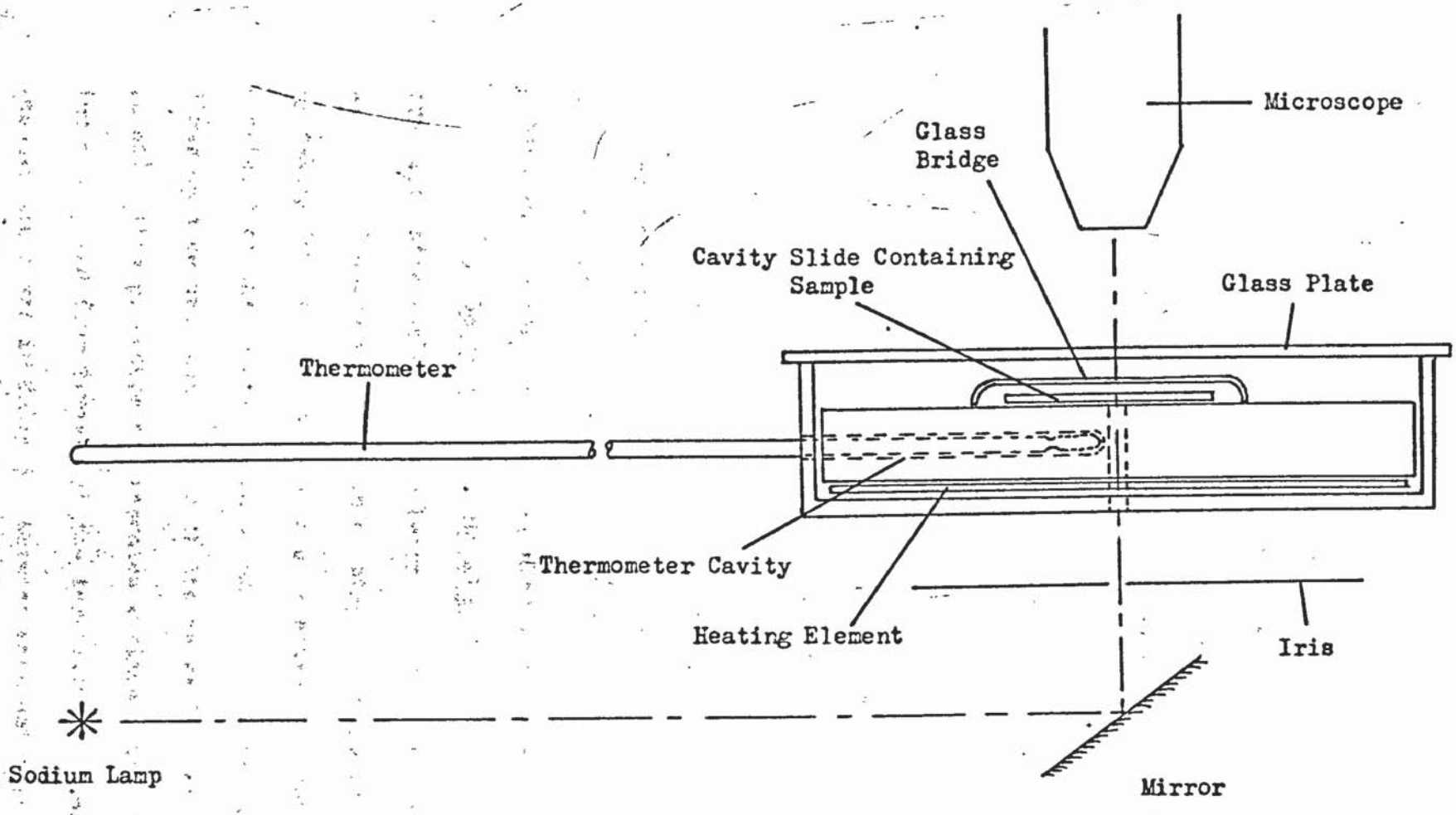


DIAGRAM OF REICHERT HOT-STAGE

FIG. 4

and liquid were covered with a cover slip taking care to exclude all air bubbles. The slide was mounted on the hot stage and the glass fragments viewed through a microscope using transmitted sodium light illumination. As the microscope objective was racked upwards a bright 'halo' of light known as the Becke line was seen to move away from the edge of the glass into the liquid. As the liquid was heated the refractive index of the glass and liquid approached the same value and the Becke line and the glass fragments disappeared. On further heating the refractive index of the liquid became lower than that of the glass and the Becke line reappeared moving into the glass. The temperatures at which the Becke line disappeared and reappeared were recorded and averaged to find the match-point temperature and this figure used to calculate the refractive index of the glass. The temperature range between the disappearance and reappearance of the Becke line was generally about 0.5°C. If the range was much over 1°C, then this usually indicated that a poor Becke line had been chosen and the readings were repeated using a second fragment.

(b) Selection of a suitable immersion liquid. The precision attainable with the Reichert hot-stage using several different liquids was determined using 1-3mg fragments of glass by taking 10 sets of readings on a selected fragment. Each set consisted of the determination of the mean temperature of the disappearance and reappearance of the Becke line (the match point); this procedure was repeated 4 times with the temperature increasing and four times with the temperature decreasing. The results are given in Table 5. Between each determination the sample was removed from the immersion liquid, blotted dry between filter papers and remounted in fresh liquid.

TABLE 5

Table of standard deviations of refractive index of glass fragments in various immersion liquids.

Clove Oil	Cargille liquid No. 1	Cargille liquid No. 2	Silicone Fluid MS710
0.000074	0.000074	0.000059	0.00002

Using crushed glass the standard deviation was determined by a different technique. A piece of plate glass approximately 1cm square was crushed in a mortar and pestle. After sieving through a BS 120 mesh sieve to remove the small pieces, a few milligrams were placed on a cavity slide and silicone oil added. The match-point was then determined by viewing the sharpest Becke line present and the procedure repeated 10 times as previously described. The standard deviation using this procedure was found to be 0.000016 when using silicone fluid type MS710.

The refractive index of liquids at various temperatures was determined by placing a few drops of liquid between the water jacketed prisms of an Abbe refractometer and circulating water through the jackets from a constant temperature water bath. The temperature of the water in the bath was measured to the nearest 0.05°C and it was assumed that there was no appreciable drop in temperature along the short piece of rubber tubing to the refractometer. The temperature was raised in approximately 5°C intervals from 20°C to 70°C allowing 10-15 minutes at each temperature. The effect of time on the refractive index of clove oil and sili-

cone fluid was examined and the results are shown in Figures 5 and 6. In addition, several batches of silicone fluid type MS710 were examined, together with several organic liquids that have been suggested by other workers[4,36]. Table 6 gives the results obtained from the various liquids examined. Temperature vs refractive index plots for silicone fluid type MS704 (which has a higher refractive index than type MS710 - see Table 6) and a Cargille liquid are shown in Figures 7 and 8.

The best straight line was fitted to the data points using the method of least squares. A Hewlett-Packard 9100B programable desk calculator was used to carry out the calculation.

4.1.3. By Using the Becke line and a Mettler Hot-stage

The Mettler hot-stage was designed primarily to determine the melting point of very small quantities of organic materials. It consists of 3 units (a) the heating compartment, (b) the control unit and (c) a set of push-buttons mounted in a separate box for recording up to 3 given temperatures. The heating compartment is shown diagrammatically in Figure 9. The glass slide containing the glass fragment in the immersion fluid is situated between two plates each of which is heated by an electric heating element. Embedded in the lower plate is a platinum resistance thermometer. The control unit compares the temperature detected by the platinum resistance thermometer with the temperature that has been set manually on the front of the control unit. Any difference is corrected electronically by altering the amount of current flowing into the heating elements situated in the plates. When the plates are at the same temperature as that indicated on the control unit, an indicator lamp lights to show

TABLE 6

Properties of immersion liquids examined

Liquid	Slope	Intercept (Temp. = 0°C)	Approx. usable range (35°C - 100°C)
Methyl Salicylate	-4.49×10^{-4}	1.545581	1.530 - 1.501
Acetophenone	-4.39×10^{-4}	1.542251	1.527 - 1.498
Chlorobenzene	-5.35×10^{-4}	1.534963	1.516 - 1.481
Clove Oil	-4.45×10^{-4}	1.543403	1.528 - 1.499
Nitrobenzene	-4.61×10^{-4}	1.561117	1.545 - 1.515
Cargille liquid	-4.08×10^{-4}	1.544184	1.530 - 1.503
Silicone oil MS710	-3.68×10^{-4}	1.543728	1.531 - 1.507
" " " " Batch 63/506	-3.71×10^{-4}	1.543642	1.531 - 1.507
" " " " " 95/925	-3.70×10^{-4}	1.543289	1.530 - 1.506
" " MS704	-4.02×10^{-4}	1.564437	1.550 - 1.524
" " " " Lot 184	-4.04×10^{-4}	1.567110	1.553 - 1.527
" " MS702 Batch 62/531	-4.00×10^{-4}	1.526225	1.512 - 1.486

THE EFFECT OF TIME ON THE REFRACTIVE INDEX VS. TEMPERATURE OF A SAMPLE OF CLOVE OIL

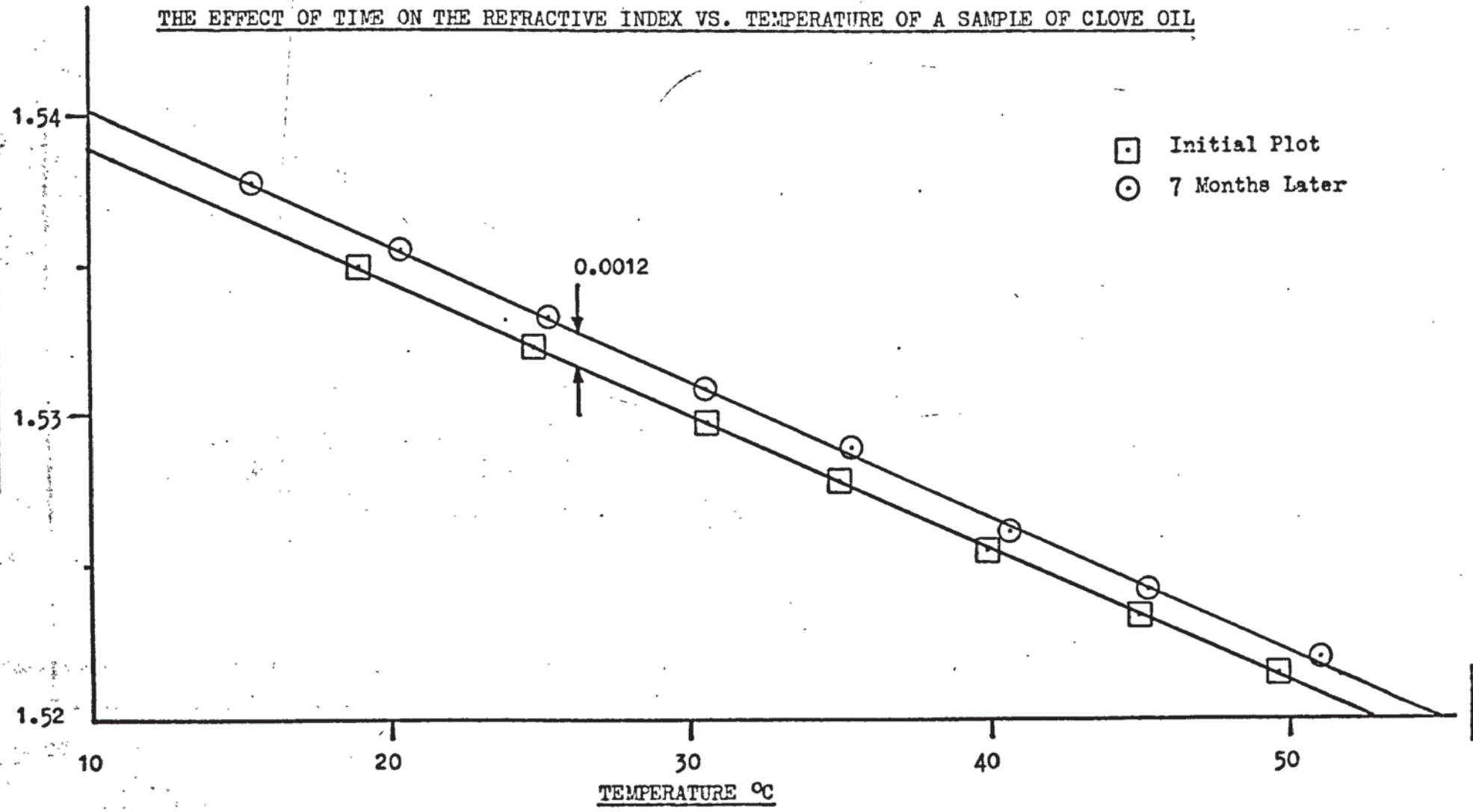


FIG. 5

THE EFFECT OF TIME ON THE REFRACTIVE INDEX VS. TEMPERATURE OF SILICONE OIL TYPE 710

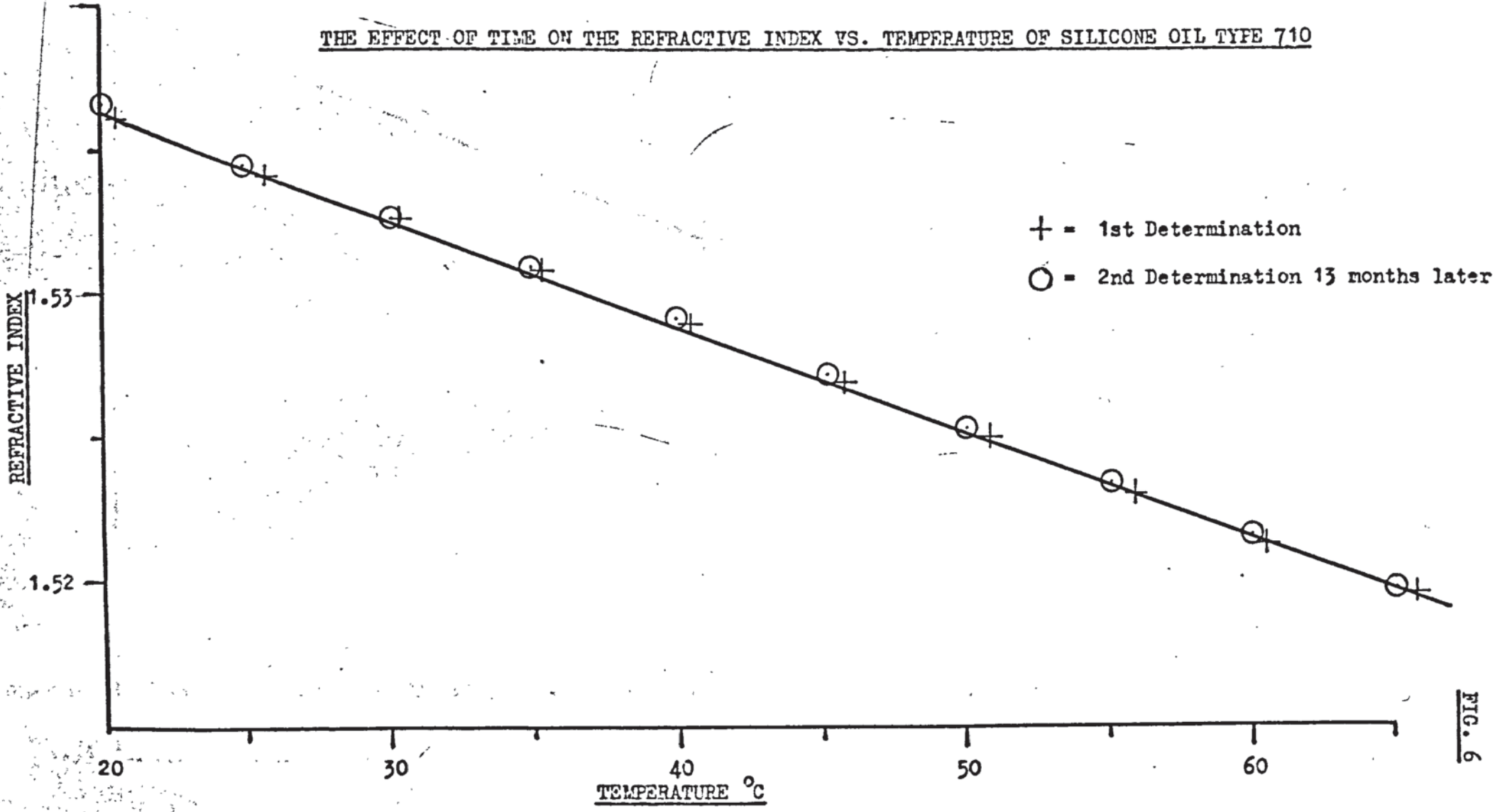


FIG. 6

REFRACTIVE INDEX VS. TEMPERATURE FOR SILICONE OIL TYPE M.S. 704

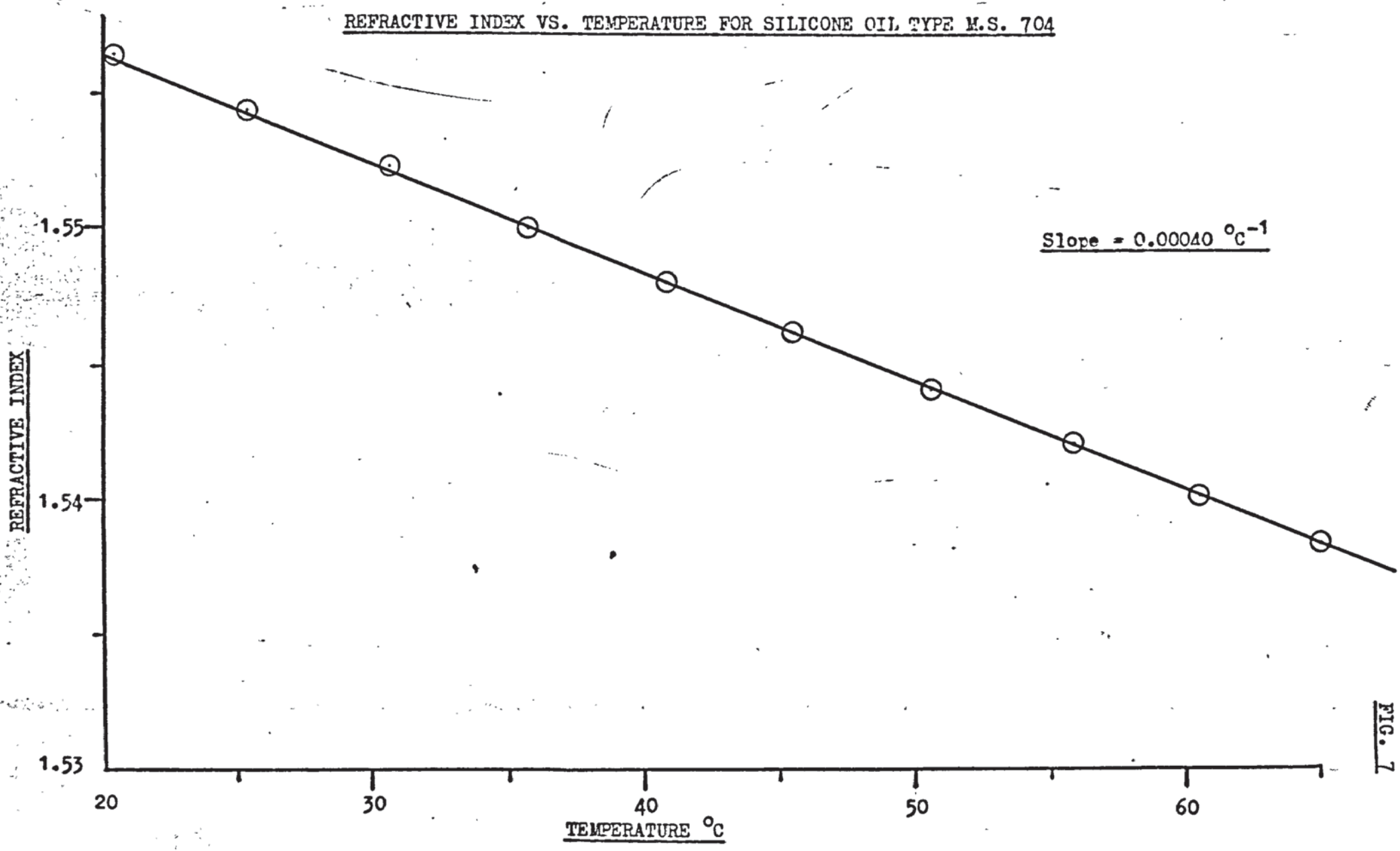


FIG. 7

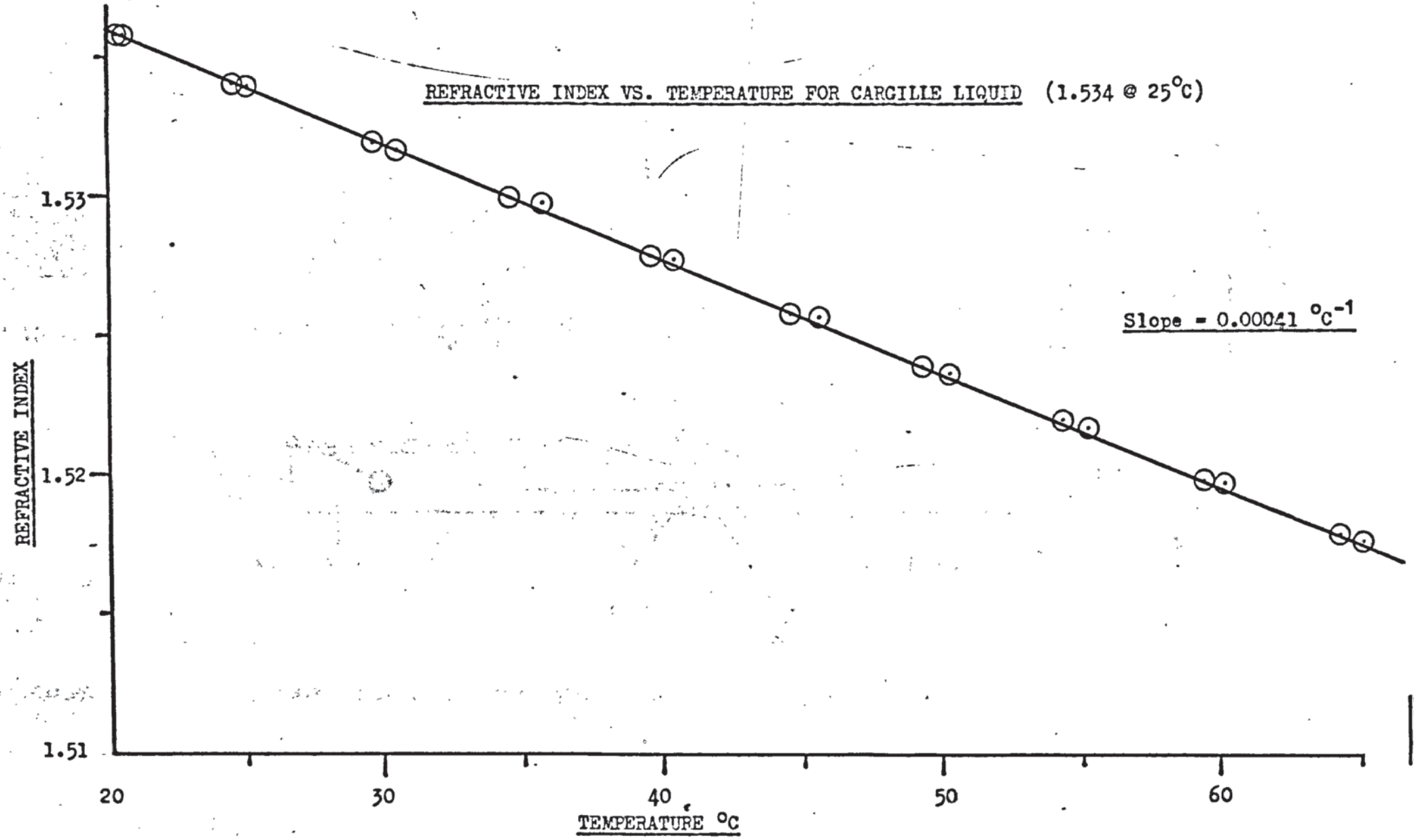
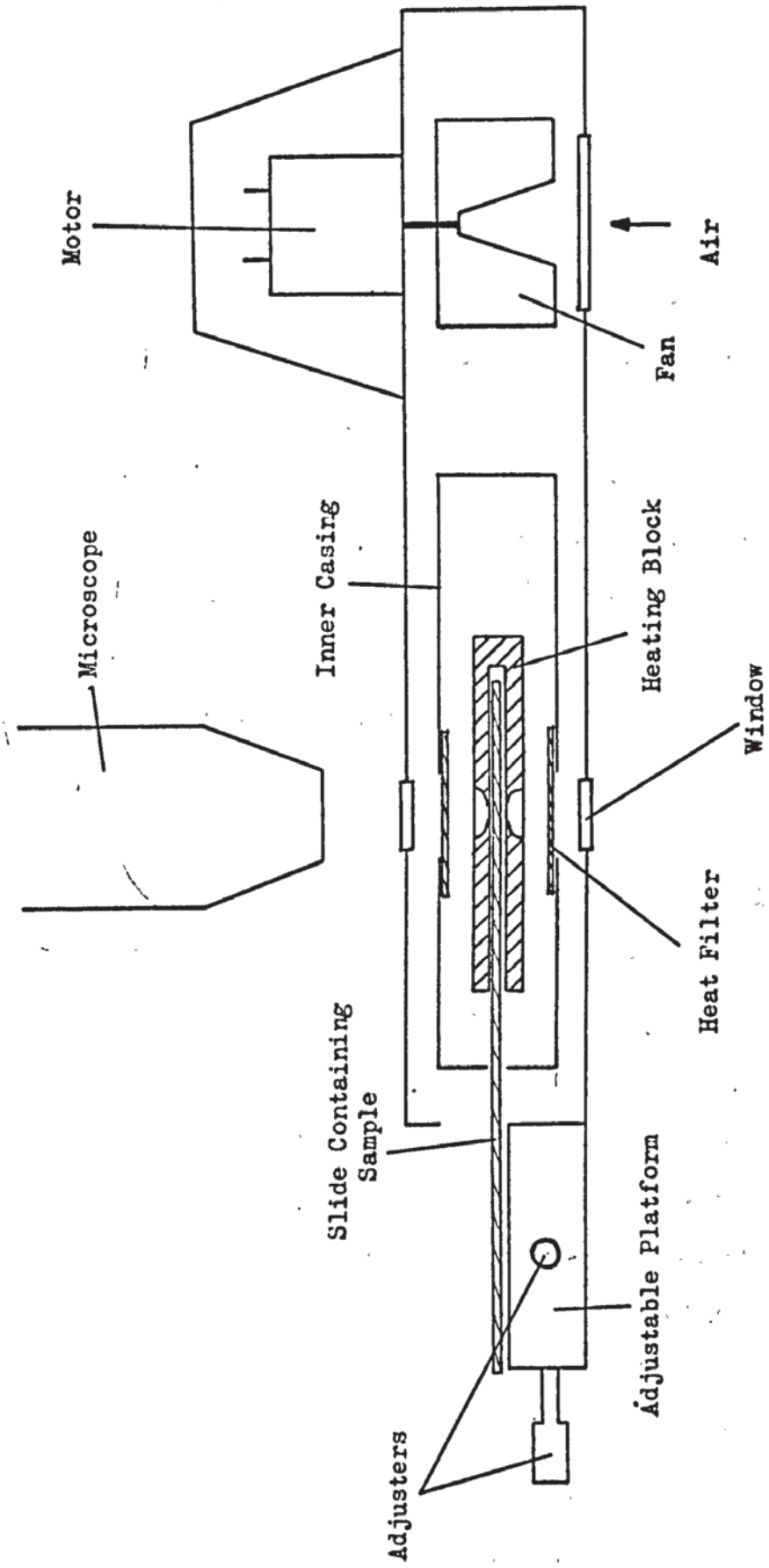

REFRACTIVE INDEX VS. TEMPERATURE FOR CARGILLE LIQUID (1.534 @ 25°C)
Slope = 0.00041 °C⁻¹
REFRACTIVE INDEX
1.53
1.52
1.51
20
30
40
50
60
TEMPERATURE °C

FIG. 8

FIG. 9



DIACRAM OF METTLER HOT-STAGE

this condition. The temperature of the hot-stage may be increased at a number of pre-set heating rates which may be selected by a series of switches on the front of the control unit. As the temperature is increasing up to three temperatures may be recorded by pressing one of the set of three push-buttons.

A slide was prepared containing 1 milligram of glass in MS710 silicone oil. The Mettler hot-stage was mounted on a Reichert Thermopan microscope and the slide was placed in position on the hot-stage. The temperature was increased and the temperatures at which the glass disappeared and reappeared were recorded. The experiment was repeated ten times for each temperature gradient using the same glass sample in each case. The results are given in Table 7. A plot of heating rate against match point temperature is shown in Fig. 10.

The temperature lag in the hot-stage was further examined by using a Mettler FP2 Rev which was an identical instrument except that it had facilities for programmed cooling. The match-point temperature of three fragments of glass was observed at five different heating rates, the observations shown being the mean of three readings. The results are shown in Table 8.

The refractive indices of several samples of glass were determined using the Abbe refractometer. Fragments of these glasses were broken off and the refractive index of these pieces also determined by the Becke line method using the Mettler hot-stage. After conversion of temperature to refractive index the reading obtained agreed well with the results obtained using the Abbe refractometer (Table 9).

A slide was prepared containing a piece of glass which gave a good Becke line. Seven people were asked to determine the

TABLE 7

Effect of Heating Rate on Mean Temperature, Standard Deviation, etc.

Temp. Grad.	Mean Temp. °C	Std. Dev. °C	Range °C	Mean of differences between readings* °C
10°C/min	76.68	0.078	0.20	1.09
3°C/min	75.17	0.048	0.15	0.86
2°C/min	74.90	0.033	0.10	0.72
1°C/min	74.68	0.042	0.15	0.58
0.2°C/min	74.47	0.054	0.20	0.34

* Mean difference in temperature between disappearance and reappearance of the Becke line.

match-point temperature on this piece at the 1°C/min heating rate. The seven people included some well used to determining refractive index by the Becke line method and some who had virtually no experience at all. The total range of results found in this experiment was 0.25°C. The range of the means of each individual operator was 0.16°C. The results are given in Table 10.

An attempt was made to check the temperature calibration of the hot-stage by the determination of the melting points of phenacetin and acetanilide. However, although the Mettler was designed for this type of measurement the melting points of organic compounds are not known accurately enough for them to be of use in the calibration of the hot-stage. Literature values of the melting points differ by more than 1°C.

THE EFFECT OF HEATING RATE ON THE MATCH-POINT TEMPERATURE

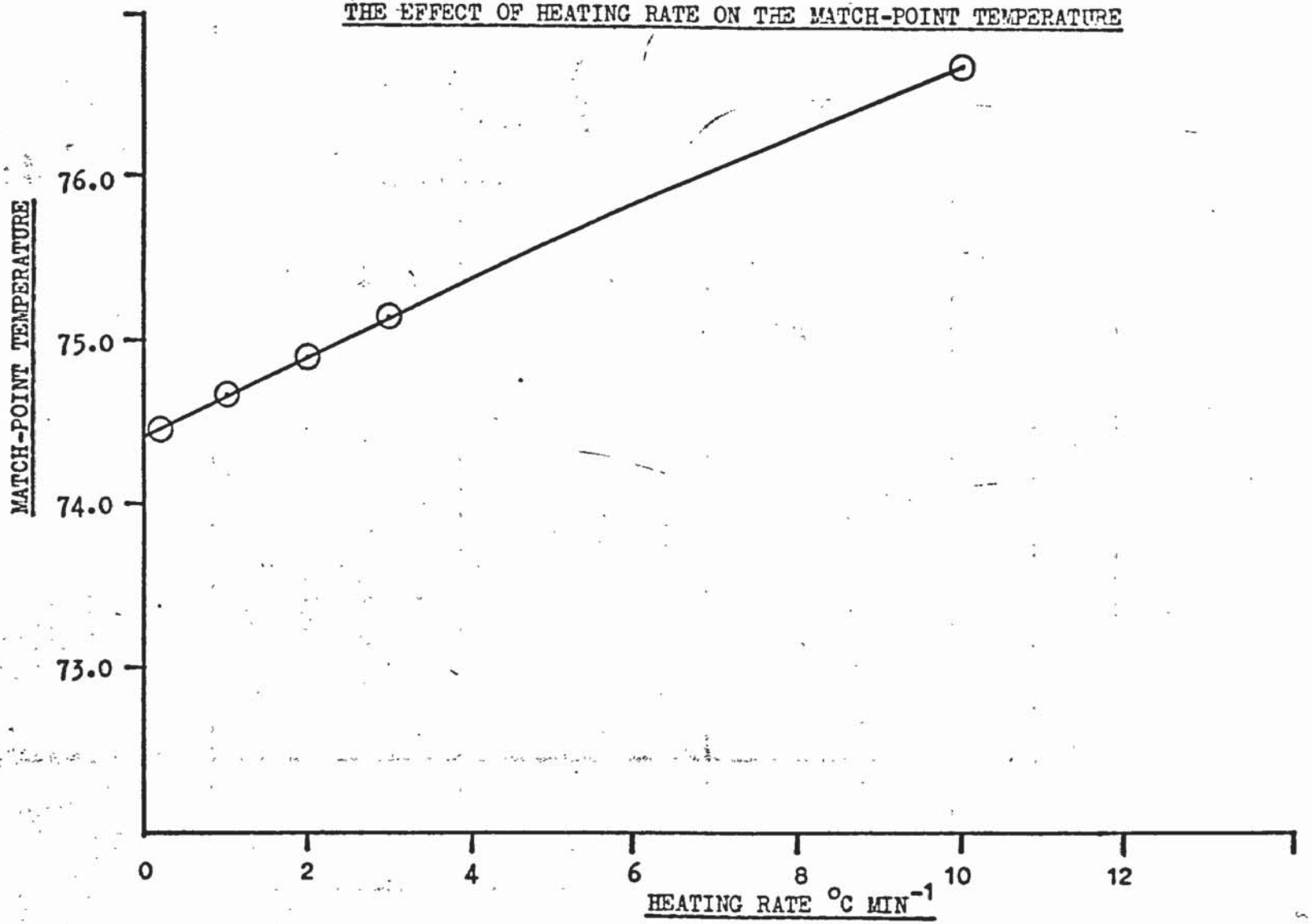


FIG. 10

TABLE 8

Temperature lag on a Mettler FP2 illustrated using 3 different fragments of glass.

		Rate of Temperature Increase $^{o}C\ min^{-1}$				
		0.2	1.0	2.0	3.0	10.0
Fragment A	Up	48.50	48.66	48.84	49.01	50.51
	Down	48.35	48.14	47.96	47.74	Unstable
	Mean values	48.43	48.40	48.40	48.38	
	ΔT	0.15	0.52	0.88	1.27	
Fragment B	Up	69.82	69.82	69.99	70.10	71.36
	Down	69.50	69.39	69.25	69.17	Unstable
	Mean values	69.66	69.61	69.62	69.64	
	ΔT	.32	0.43	0.74	.93	
Fragment C	Up	87.08	87.28	84.40	87.62	88.84
	Down	86.95	86.77	86.58	86.39	84.96
	Mean values	87.02	87.03	86.99	87.01	87.40
	ΔT	0.13	0.51	0.82	1.23	4.88

TABLE 9

Refractive Index Determined by the Mettler Hot Stage and the Abbe refractometer

Method	1st Sample	2nd Sample	3rd Sample
Abbe mean of 8 readings	1.5170	1.5160	1.5150
Mettler mean of 3 readings	1.51691	1.51584	1.51583

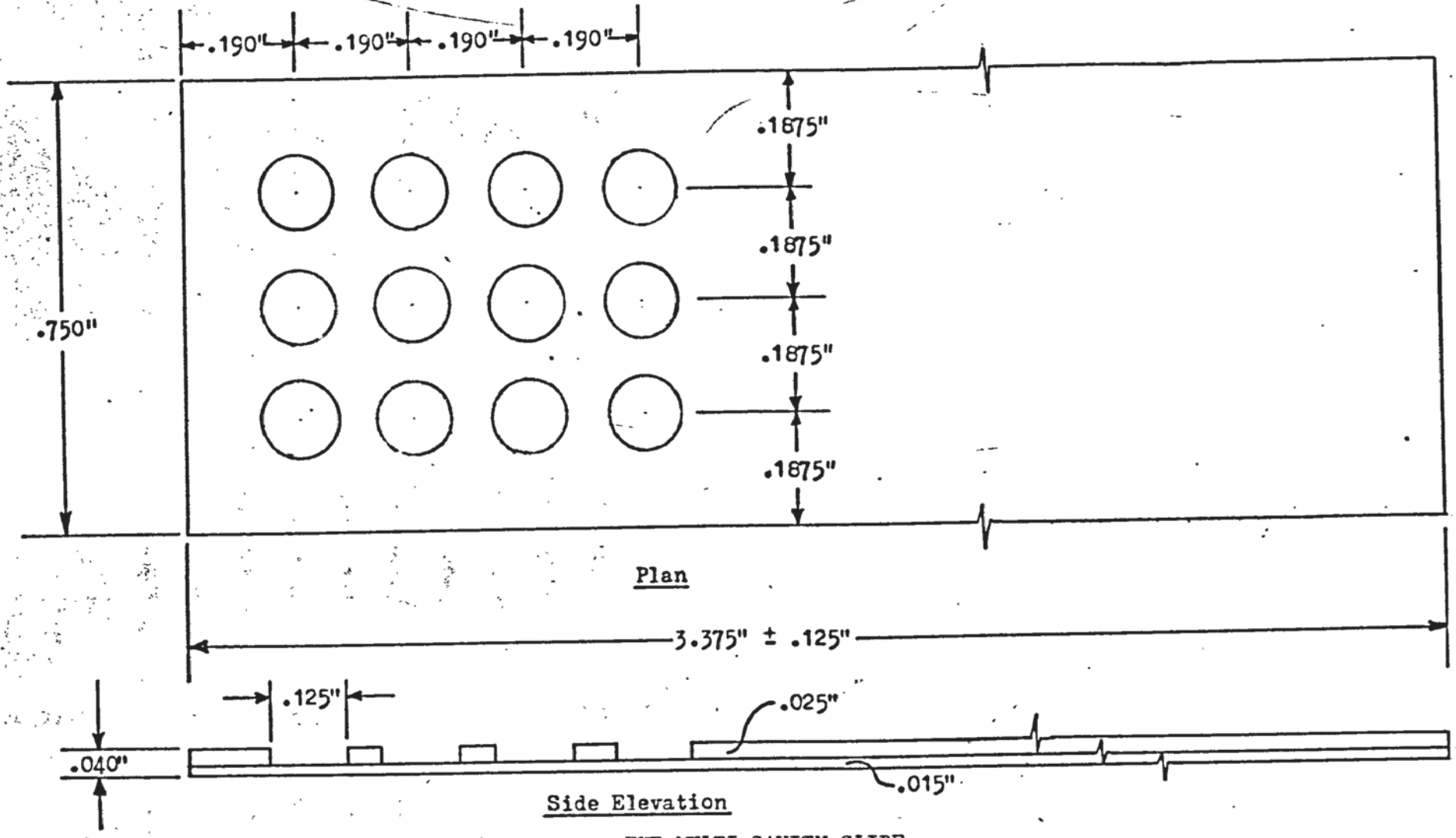
TABLE 10

Match Point Temperature on the Same Piece of Glass by different operators

Operator	Experience	Mean
A	experienced	73.44
B	limited experience	73.47
C	limited experience	73.43
D	no experience	73.52
E	experienced	73.38
F	experienced	73.39
G	experienced	73.54
	Mean	73.45

4.1.4. The Multi-Cavity Slide

A multi-cavity slide for use with the Mettler hot-stage was designed and constructional details are shown in Figure 11. This slide allowed 10 control samples and the crime sample to be mounted together on the same slide so that a statistical assessment of the control sample could be made. The slide was made by drilling the holes in a piece of 0.125" glass and then grinding and polishing the glass down to the required thickness. This glass was then stuck to a piece of thin plate glass using an epoxy resin (type NE 560). The limiting factors in designing the slide were the size of the hot-stage and the distance between the holes required to prevent inter-hole cracking.



THE MULTI-CAVITY SLIDE

FIG. 11

4.2 DISCUSSION

The Abbe refractometer was shown to be suitable for use with unpolished glass samples. Table 4 shows that by taking four readings on each face and determining the average the precision of the method is increased over taking one reading on a polished sample. Four readings on an unpolished rough cut piece of glass yields a standard deviation of better than 0.0001.. Therefore, if this technique is followed, the Abbe refractometer is suitable for determining the refractive index of survey samples with a standard deviation of 0.0001.

The Reichert hot-stage is an instrument that has been shown to be capable of a precision of 0.00002[32]. However, the Mettler FP2 hot-stage is a more convenient and faster instrument to use. The precision in terms of standard deviation on repeat readings of the refractive index on the same sample of glass was found to be approximately 0.00002. The results obtained by different operators corresponds to an agreement of 1 in the fourth place for refractive index. However, examination of Figure 10 shows that there is a thermal lag in the system which causes the temperature indicated on the Mettler control unit to be higher than the temperature in the hot-stage when the temperature is increasing. At the $1^{\circ}C\ min^{-1}$ heating rate the temperature lag varied between $0.22^{\circ}C$ and $0.26^{\circ}C$ with a mean value of $0.24^{\circ}C$ for both instruments examined, but this figure will probably vary according to the type of microscope slide used. This lag may appear to be significant when compared with the range of temperatures covered with a particular immersion fluid. However, if a comparison is being made between two glass fragments, the

temperature lag in each experiment will cancel out and no correction need be made. If the refractive index of a fragment is to be compared to a given distribution of glasses (section 6), then it will depend on the way the refractive index of the distribution was measured whether it will be necessary to apply a correction for temperature lag. If the survey of refractive indices has been made using a Mettler hot-stage any temperature lag will again cancel out, but if the survey has been made using a refractometer the correction will be necessary. The magnitude of the correction in terms of refractive index will depend on the temperature coefficient of refractive index for the immersion fluid. For example, with MS710 the coefficient is $-0.00037°C^{-1}$ and therefore, the temperature lag in terms of refractive index is -0.000089. Examination of Figure 12 shows that the only region where the lag is likely to be significant is in the region of modern glass viz. around a refractive index of 1.516. In all other regions slight inaccuracies in the determination of refractive index is unlikely to effect the value obtained for the probability of occurrence.

The outstanding advantage of the Mettler hot-stage is the programmed temperature increase which keeps the heating rate constant at any temperature for any given rate and requires no adjustment so that the operator can concentrate on determining the match point temperature. In addition, the operator only has to press a button to record a temperature so that it is not necessary for him to interupt his observation of the glass.

The multi-cavity slide was found to be extremely useful and was used extensively in the clothing survey. The diameter of the cavities proved to be quite adequate for normal use and in addition is was found to be unnecessary to use cover slips with

the slides providing the determination was made immediately after mounting. A number of these slides have been made and issued to regional Forensic Science Laboratories.

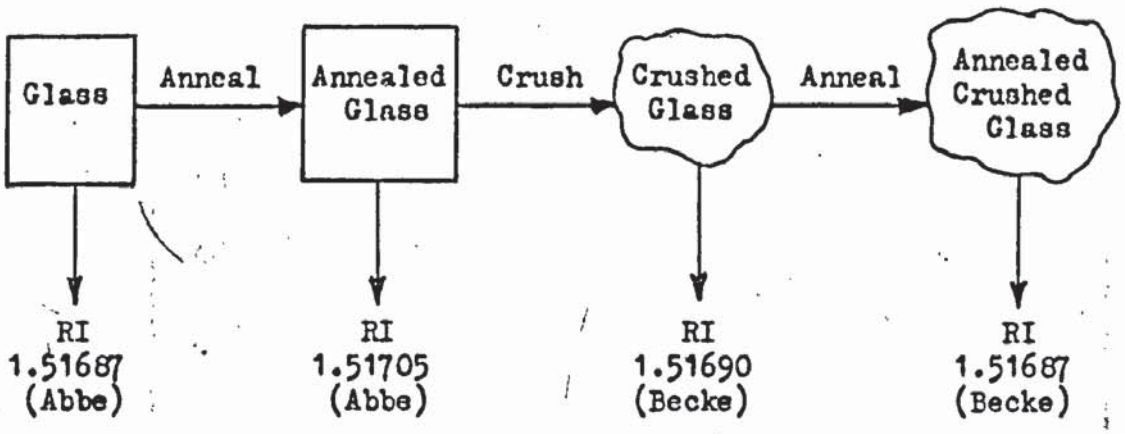
For good sensitivity to small changes in refractive index it is necessary to use a liquid whose refractive index changes only a small amount with temperature, that is, one which gives the least slope when its refractive index is plotted against temperature. In these experiments silicone fluid type MS710 was shown to have the smallest slope, but it was only slightly less than other liquids. The refractive index of clove oil was shown to alter with time in contrast to silicone oil whose refractive index was remarkably constant. From the graphs of temperature vs refractive index it is clear that the assumption that there was no temperature difference between the water jacketed prisms and the water bath was reasonable because any temperature lag would cause curvature of the lines.

During the precision experiments on the Reichert hot-stage, clove oil and the Cargille liquids tended to mist up the cover glass over the microscope slide making clear observation of the sample impossible. This effect was completely absent when using either MS710 or MS704 silicone fluid. For the above reasons silicone fluid type MS710 or MS704 was used for all subsequent work.

4.3 EFFECT OF CRUSHING AND PARTICLE SIZE

4.3.1. Experimental

The effect of crushing upon the physical properties of glass was examined using the Abbe refractometer and the Mettler hot-stage. The refractive index of a piece of modern sheet glass 1.0cm x 1.5cm was determined on the Abbe refractometer before and after annealing at 600°C. The glass was crushed and the refractive index determined by the Becke Line technique as previously described. The crushed glass was then re-annealed and its refractive index determined. A flow chart for the experiment and the results are shown in the accompanying diagram.



The precision of the readings of refractive index on the Abbe refractometer and the Mettler hot-stage was 0.00010 and 0.00002 respectively.

The effect of particle size on the refractive index of glass was examined by crushing a 3cm x 3cm piece of plate glass and sieving out certain fractions as shown in Table 11. Ten samples from each fraction were then mounted in the multi-cavity slide and one reading taken on each sample. The results are shown in Table 11.

TABLE 11

The effect of particle size on match-point temperature

B.S. Mesh	Mesh Size (μm)	Median Size (μm)	Size Range (μm)	Mean Match-point Temperature °C	Standard Deviation °C
8	2000	1840	320	-	-
10	1680				
16	1000	925	150	74.14	0.09
18	850				
25	600	550	100	74.20	0.07
30	500				
36	420	387.5	65	74.19	0.09
44	355				
52	300	275	50	74.22	0.05
60	250				
85	180	152.5	55	74.20	0.07
120	125				
240	63	54	18	74.26	0.12
350	45				

4.3.2. Discussion

In the examination of the effect of crushing glass the annealing procedure followed should have removed all the strain from this type of glass. Two methods have been used to determine the refractive index and of the two the Becke line technique is the more precise. Therefore, the most reliable conclusions can be obtained by studying the results using this method. The difference in the refractive index obtained before and after the second annealing was 0.00003. Because each determination was carried out in duplicate and the average taken, the standard deviation becomes $\frac{0.00002}{\sqrt{2}} = 0.000014$. Therefore, the two results are a little over 2 standard deviations apart which is not significant. The standard deviation of the results obtained from the Abbe refractometer is 0.0001 and the difference the refractive index obtained on the Abbe refractometer and the refractive index obtained using the Becke line technique after the glass had been crushed was 0.00015, that is, 1.5 standard deviations. Again this is not significant. Therefore, these results show that there is evidence that crushing does not introduce any detectable strain into the glass.

In the examination of the effect of particle size on the match-point temperature the first and last fractions gave poor Becke lines and this would partially explain the slight difference between these two results and the remainder. The four remaining results show that in the range 125-1000μm the match-point temperature is not affected by the size of the particle.

5. THE VARIATION IN DENSITY AND REFRACTIVE INDEX ACROSS A PANE OF GLASS

A knowledge of the extent of any variation in physical properties across a pane of glass is necessary for two reasons. Firstly, it is important to be aware of any heterogeneity when comparing the crime sample to the control or the crime sample may be classified as different even though, in fact, it originated from the same pane of glass. Secondly, it is necessary to know the variation which is likely to occur over an area of glass before any survey work may be carried out. Clearly any large variation in physical properties across a pane of glass may necessitate more than one sample being taken from each pane in the survey. The object of this work was to determine if there was any regular variation in physical properties across a pane of modern glass using large samples (20mm x 15mm) and to determine the extent of any microheterogeneity using milligramme size samples.

The magnitude of the heterogeneity is measured by determining the standard deviation of a given set of results. Other workers[53,78] have used the standard deviation of a series of measurements of refractive index as a measure of the heterogeneity of glass samples and Parker[60,61] uses the same term when he considers heterogeneity (which he calls intrinsic variation). This technique measures the variation due to both the experimental error and the heterogeneity in the glass, but these two effects may be separated using the theory of errors[94]. In addition, a statistical technique known as the Analysis of Variance is used to test some of the results obtained using the Mettler hot-stage.

5.1 EXPERIMENTAL

5.1.1. Sampling

Two sheets of glass (2ft. x 3ft.) were purchased from a local supplier as 0.25" plate and 0.125" sheet. Both specimens had been manufactured about 1967. Each sheet was cut into 25 equal sections, each measuring approximately 180mm x 120mm.

5.1.2. Refractive Index

A 20mm x 15mm sample was cut from each section and the refractive index determined by taking eight measurements on each sample; one through each edge of the two faces. The measurements were taken on an Abbe refractometer using the method described in section 4.1.1. Each face was measured at a different time and the results were taken in random order (from random number tables). The standard deviations calculated for each pane of glass are given in Tables 12 and 13. The corresponding errors are given in Table 4 in section 4.1.1.

The standard deviations obtained justify a closer examination of the local refractive index variation across the sheets of glass to study microheterogeneity. Two to three milligramme samples were, therefore, prepared by taking a sample of glass from each section and crushing this in a small agate mortar and pestle. The crushed glass was mounted on a cavity slide in silicone fluid type MS710 and the determination made using a Reichert Hot-stage in the manner previously described. A summary of the results is shown in Table 14.

The standard deviations given in Tables 14 and 15 show the actual variation across the pane of glass after subtracting the error of the method by using the rule for the addition of variances viz:-

TABLE 12

Variation across 0.25" plate glass using the Abbe refractometer

	No. of Results	Standard Deviation
All readings taken on each sample	200	0.00012
On means of readings on each face (means of 4 readings)	50	0.00007
On means of readings on each piece (means of 8 readings)	25	0.00005

TABLE 13

Variation across 0.125" sheet glass using the Abbe refractometer

	No. of Results	Standard Deviation
On means of readings on each sample face (means of 4 results)	50	0.00006
On means of readings on each sample (means of 8 results)	25	0.00004

TABLE 14

Summary of refractive index results from Becke line experiments using the Reichert hot-stage and crushed glass in type MS710 silicone oil

	Standard Deviation	Observed Range
Variation across 0.25" plate (25 samples)	0.00005	0.00022
Variation across 0.125" sheet (25 samples)	0.00007	0.00034

TABLE 15

Actual variation across sheet glass using Mettler FP2 and MS710 silicone oil

	Standard Deviation
10 Repeat determinations on a single fragment	0.000015
Variations over 0.125" sheet glass (100 readings)	0.000022

$$S^2_{tot} = S^2_{error} + S^2_{glass}$$

where S^2_{tot} = total measured variance

S^2_{error} = variance due to error in method

S^2_{glass} = variance due to variation in glass.

The pane of sheet glass was also examined for variation using a Mettler FP2 hot-stage. Four separate samples were taken from each of the 25 sections of glass and a separate determination made on each yielding 100 individual readings. One reading with the temperature increasing was taken in each case and in addition ten determinations were made on a single fragment to determine the error involved in remounting the glass as previously described in section 4. The results are given in Table 15.

Ten sections of sheet glass were selected from the 25 using random number tables. One small fragment weighing about 2 mg was taken from each of the ten sections and ten determinations of the match point made on each using the Mettler hot-stage. The results were analysed by using Single factor Analysis of Variance[91,96]. Table 16 shows a summary of the results. From the Table, F, the variance ratio was calculated to be 4.81. From tables, the value of F at the 0.1% significance level is 3.24 and, therefore, the difference between the two variances is highly significant.

TABLE 16

Variation across sheet glass using the Mettler hot-stage and MS710 silicone oil. Results from the Analysis of Variance

Source of Variation	Sum of Squares	Degrees of Freedom	Variance Estimate
Between samples	1,199	9	$\frac{1,199}{9} = 133.2$
Within samples	2,495	90	$\frac{2,495}{90} = 27.72$
Totals	3,694	99	

5.1.3. Density

The apparatus used to determine the density spread in the glass has been described previously.

The density spread over the pane was determined by placing one 5mg fragment of glass from each section into the test tube. Beforehand each fragment was examined under a microscope to ensure that it was free from visible cracks and flaws in the surface. The temperature of the water bath was increased until all the fragments had sunk and then lowered at about $0.03^{\circ}C\ min^{-1}$ and the temperature noted at which the fragments passed a line marked on the side of the test tube. The procedure was similar to that used by Knight[16]. The difference in temperature between the first and last fragments was the range and the density was calculated from the determined temperature coefficient of density of the liquid.

The precision of the method was determined by placing two 5mg fragments of glass in the test tube and observing the

temperatures at which they passed the line inscribed on the side of the test tube. The difference between these two temperatures was noted and the experiment repeated 13 times. The standard deviation of the difference between the two temperatures was found to be 0.00016g cm^{-3}.

The experiments were then repeated using 0.5g samples taken from each section of the glass in a 30mm x 300mm test tube.

In order to determine whether occluded air in the glass was affecting the results, a number of experiments were performed in which the solution and the 5mg samples were cooled to -70°C and degassed by the freeze-thaw technique.

Differences in the thermal history of the glass may cause variations in its physical properties and these may be removed by annealing. The effect of annealing prior to analysis was investigated by maintaining the glass at 550°C for 1 hour and then cooling slowly.

The results are given in Table 17.

Attempts to fire polish the glass to remove invisible surface flaws were unsuccessful.

TABLE 17

Range of density between lightest and heaviest glasses under various conditions in $g\ cm^{-3}$

	Sheet Glass			Plate Glass		
	Before Annealing	After Annealing @ 550°C	After Annealing @ 700°C	Before Annealing	After Annealing @ 550°C	After Annealing @ 700°C
Normal (5mg samples)	0.0006	0.00052	0.00049	0.00059	0.00041	0.00113
After freezing and pumping (5mg samples)	0.00032	0.00060	---	---	0.00046	0.00073
Normal 0.5g samples	0.00028	---	---	---	---	---

5.2 DISCUSSION

5.2.1. Refractive Index

Examination of Tables 12 and 13 shows that when using an Abbe refractometer, the variation over the pane is no greater than the error in the method, as described in Section 4.1.1.

A greater error was observed on the plate glass measurements than on the sheet glass. This was almost certainly due to the fact that it is easier to cut small pieces of sheet glass with a clean edge than it is plate.

For samples measuring 10mm x 15mm it may be concluded that it is not possible to detect a variation across a 3ft. x 2ft. pane using this apparatus. However, it is possible that a variation may be detected by using a precision refractometer and polished samples.

Examination of Tables 14 and 15 show that the variation across the pane was larger than the error in the method.

The results obtained on the Mettler hot-stage confirm that there is a variation in refractive index over a pane of sheet glass. However, the variation is small and the discrepancy between the results obtained on the Reichert hot-stage and those obtained on the Mettler could be due to actual random variations in the glass.

The analysis of variance showed a statistically significant difference in the refractive index of samples taken from different points in the glass. There was no evidence of a gradual change of refractive index across the two sheets of glass.

5.2.2. Density

The standard deviation of the difference in density between two 5mg fragments of glass was found to be 0.00016g cm^{-3}. It is clear that this figure includes errors involved in the measurement of each individual fragment and to calculate the error due to a single sample it is necessary to refer each to an arbitrary fixed standard. The standard deviation of the density of each fragment may then be calculated using the rule for the addition of variances. The result gives a standard deviation of 0.00011g cm^{-3} for individual fragments and this figure must then be compared with the value of 0.0006g cm^{-3} obtained for the density range of sheet glass. Simple probability theory associated with the normal distribution shows that given a standard deviation of 0.00011g cm^{-3} the probability of obtaining a range of values of 0.0006g cm^{-3} in 5 independent experiments is infinitely small. Therefore, the results demonstrate that a variation in density across the panes of glass may be detected. Because of the nature of the experiment it is not possible to be specific about the magnitude of the heterogeneity from the density experiments alone.

The standard deviation of the density obtained on 5mg fragments of glass is marginally higher than the value of 0.00010g cm^{-3} that other workers have obtained on pieces of glass weighing 1.0g to 2.5g[16]. However, it is well known that the precautions that must be taken in a density determination and the difficulty of the determination increase with decreasing sample size[18]. The results indicate that with samples weighing 5mg the effect of small sample size is beginning to become noticeable.

Experiments have shown that annealing is of little help in reducing the density spread. In addition, the results obtained after freezing and pumping are very similar to the results obtained from experiments carried out in the normal manner, and this suggests that the amount of occluded air on the surface of the glass fragments is small. The wide range of results obtained after annealing the plate glass at 700°C is surprisingly large and difficult to interpret.

There are several well known equations relating refractive index and density, but Sun, et.al.[49] have pointed out the problems in obtaining a general equation to cover the relationship between these two parameters when applied to glass. Ritland[79] has found that a sample of a borosilicate crown glass subjected to various annealing treatments followed most closely the Newton-Drude formula.

To determine the expected change in density from a known change in refractive index, either the Newton-Drude equation or the Lorentz-Lorenz equation may be used. The average result using these two equations shows that for a glass with a refractive index of 1.5160 and a density of 2.4831g cm^{-3}, a 0.0001 change in refractive index should result in a 0.0005g cm^{-3} change in density.

Using this data, it may be seen from the results obtained on the Reichert hot-stage given in Table 14 that the density range, calculated from the refractive index, (6 standard deviations) would be expected to be 0.001g cm^{-3} for plate glass. This is somewhat larger than the measured variation of 0.0006 g cm^{-3} (Table 17).

From Table 15 the standard deviation for the variation in refractive index across the sheet glass is 0.000022 measured on the Mettler FP2 hot-stage. Therefore, 99.7% of the samples would be expected to fall in the range 0.000132 which on conversion to density yields a value of 0.00066g cm^{-3}. The value obtained experimentally was 0.0006g cm^{-3} (Table 17).

The density range on the 0.5g samples correspond to a calculated refractive index range of 0.00005 and confirms the conclusions reached above that it is impossible to detect a variation across the pane of sheet glass that was examined using an Abbe Refractometer measuring to the fourth decimal place.

It is clear that a variation in density and refractive index is detectable in the two sheets of glass examined. It is not possible to say whether these panes of glass were 'typical' of modern glass production, but there is no reason to suspect that they were not.

The variation in refractive index and density obtained across the glass examined is small when compared to the total range of values found in glass population studies. However, the size of the variation may well vary according to the age of the glass, and it is probable that older glasses would show larger variations.

This study of the heterogeneity of flat glass has shown that a variation in refractive index and density may be detected across a pane of flat glass using the methods described in earlier sections. Therefore, as far as forensic science is concerned for the examination of current production glass, the development of more sensitive techniques for the measurement of

refractive index and density are not necessary.

The intrinsic variation in the physical properties of glass from a single pane should be considered when making a comparison of two samples of glass. However, it has been shown that the variation is not large and, therefore, it need not be taken into account when conducting surveys of large numbers of glasses, i.e. only one sample need be taken from each pane of glass sampled.

6. SURVEYS OF GLASS SAMPLES

6.1 SURVEY OF GLASSES FROM THE SCENES OF FIRES

6.1.1. Experimental

The Atomic Weapons Research Establishment under contract to the Home Office undertook a nation-wide survey of window glasses and in order to obtain a representative, random selection of this type of glass, ninety-four fire-brigades throughout England and Wales were asked to supply samples of window glass broken at a pre-determined number of fires. Each brigade was asked to provide a certain number of samples which was determined on a proportionate basis to the population covered by each brigade in England and Wales, as shown in Fire Service Statistics[86]. Sample envelopes on which was printed a short questionaire asking for details of the age and type of building from which the glass samples were obtained were sent to each brigade. The Chief Officers of each brigade were asked to distribute the sample envelopes so that each full time station within the brigade provided a sample of broken window glass from each of two separate fires. It was requested that single pieces of glass not more than a few square inches in size should be picked up from window glass broken in some way during a fire, but not, if possible, affected by the intense heat of the fire. The samples were collected between August 1968 and May 1969.

A total of 1272 samples were requested from the fire brigades and 939 samples were received for analysis.

The samples were cleaned in hot concentrated nitric acid, rinsed in distilled water and dried. Pieces of glass measuring approximately 20mm x 20mm were cut from the larger samples and the refractive index of the pieces which had smooth

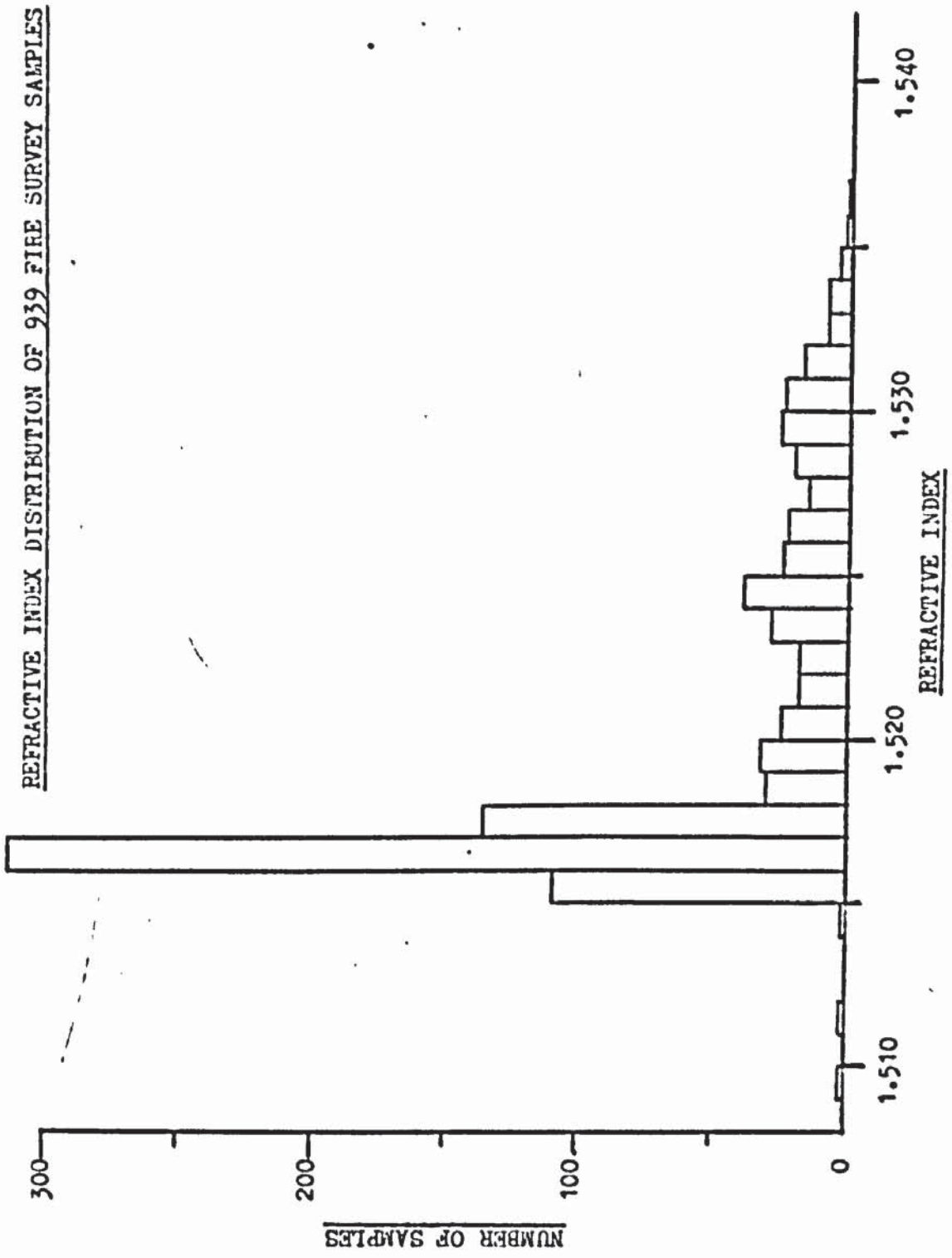
undamaged surfaces was measured on a Hilger and Watts Abbe refractometer, as described in section 4.1.1. Eight readings were taken on each piece and the results averaged arithmetically.

The refractive index of the patterned or damaged glass and those samples which gave a poor reading using the Abbe refractometer was determined by the Becke line method using a Mettler FP2 hot-stage (see section 4.1.3). One reading was taken on each sample using silicone fluid type MS710 as the immersion liquid.

The refractive index of 657 samples was determined using the Abbe refractometer and of 282 samples using the Mettler hot-stage. A histogram showing the distribution of frequency against refractive index of all 939 samples examined is shown in Fig. 12.

Of the 282 samples whose refractive index was determined using the Mettler FP2 hot-stage, 128 were patterned or frosted glass, 129 contained fine cracks characteristic of heat damage and the remaining 25 had previously given variable readings on the refractometer or failed to give a sharp cut-off between the light and dark zones in the refractometer telescope. A χ^2 test carried out between the undamaged samples and those samples showing signs of heat damage gave a value of χ^2 of 7.01 (four degrees of freedom). The value from Statistical Tables[87] at the 10% level is 7.78 and, therefore, a value of χ^2 as high as 7.78 would be obtained once in every ten trials purely by chance. Hence there is no evidence of a statistical difference between results obtained by the two techniques.

FIG. 12


REFRACTIVE INDEX DISTRIBUTION OF 939 FIRE SURVEY SAMPLES
NUMBER OF SAMPLES
300
200
100
0
1.510
1.520
1.530
1.540
REFRACTIVE INDEX

The density of the glasses was determined on samples weighing 15g or over using the method described in section 3.1.2. The density of 338 samples was determined in duplicate by this method. A histogram showing the frequency distribution against density is shown in Figure 13.

The thickness of pieces of glass which had smooth undamaged surfaces was measured to the nearest 0.05mm using a vernier caliper gauge. Only 850 were suitable for thickness measurement, the remainder being either frosted or patterned glass. A histogram showing the frequency distribution of the thickness is shown in Figure 14.

When examined under ultra-violet light, glass made by the float process fluoresces on the side which has been in contact with the molten tin. Each sample of glass was examined on both sides for fluorescence using a Camag Universal UV lamp (TL-900/U) at 254nm. The presence of tin was detected by adding one drop of hydrofluoric acid (40%) followed by 1 drop of a 0.1% solution of cacotheline in water to the glasses on the side which showed fluorescence. Table 18 shows the colour of the fluorescence and the reaction to cacotheline of those samples exhibiting fluorescence at 254nm.

The refractive index distribution of 400 glass samples taken from buildings with an estimated construction date prior to 1900 is shown in Figure 15. Figure 16 shows the refractive index distribution of 263 samples from buildings with an estimated construction date between 1901 and 1944 and Figure 17 shows the refractive index distribution of 241 samples taken from buildings with an estimated construction date between 1945 and 1969. In

DENSITY DISTRIBUTION OF 338 SAMPLES OF WINDOW GLASS BROKEN IN FIRES IN ENGLAND AND WALES

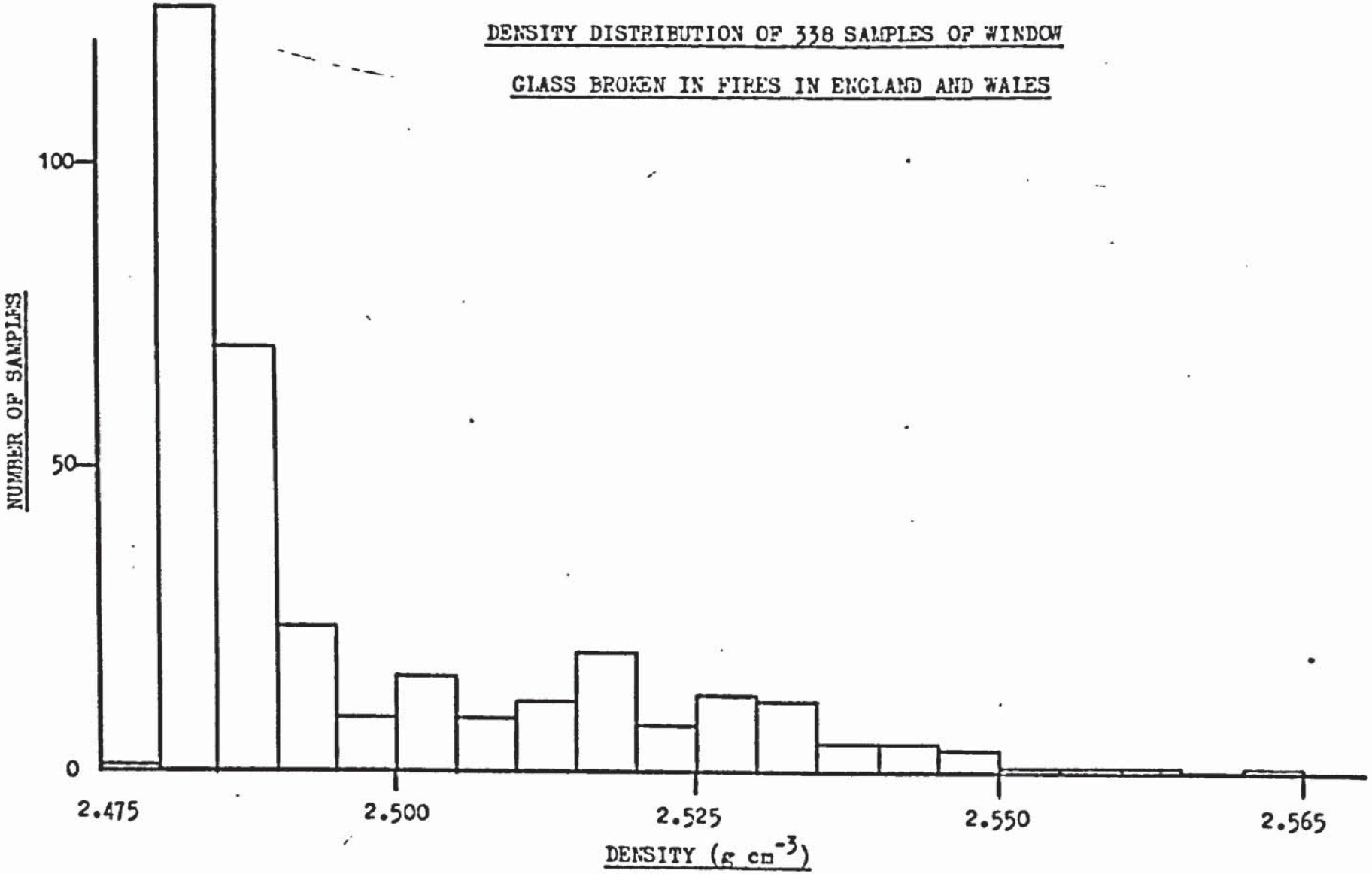


FIG. 13

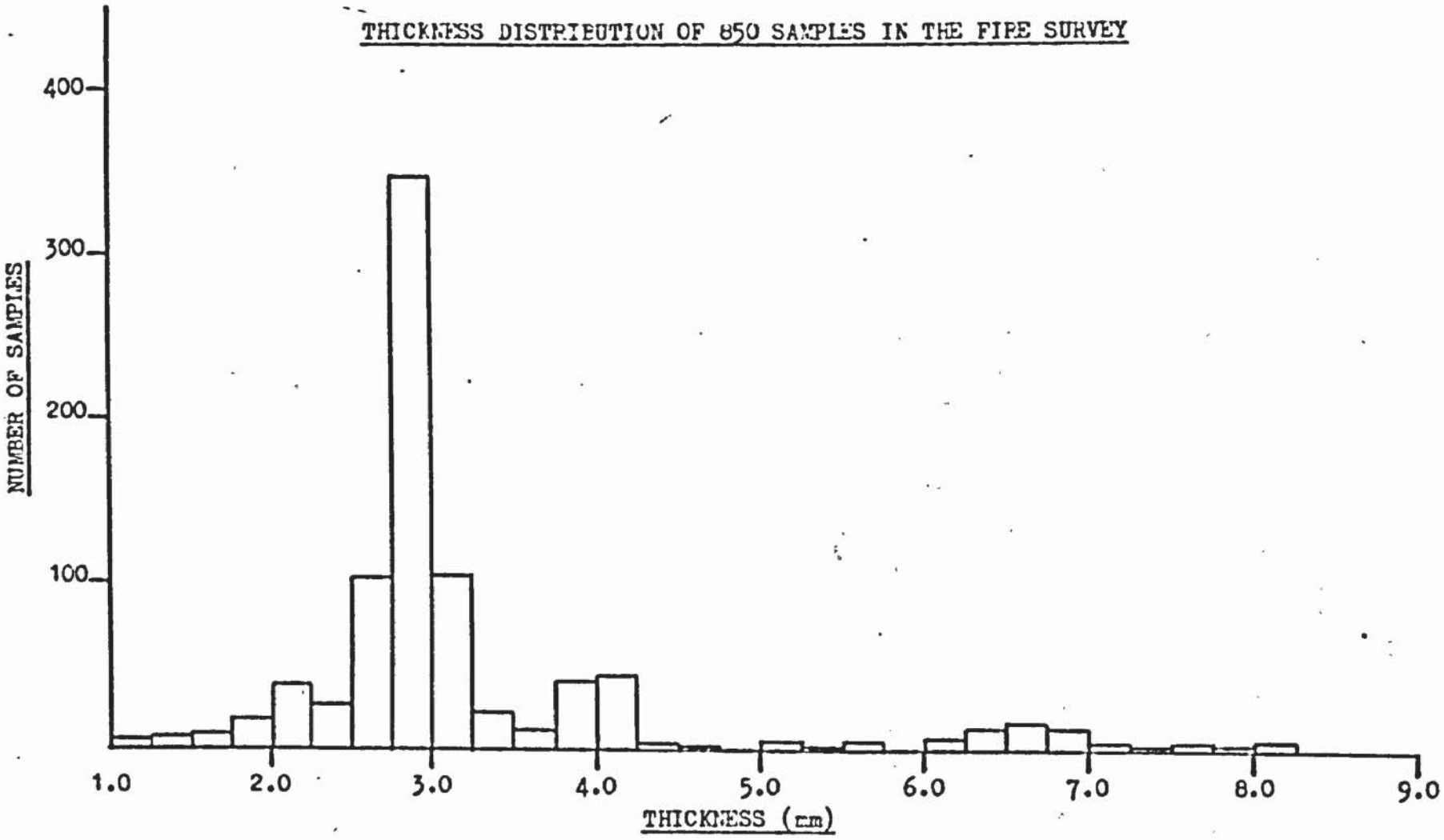

THICKNESS DISTRIBUTION OF 850 SAMPLES IN THE FIRE SURVEY
NUMBER OF SAMPLES
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
THICKNESS (mm)

FIG. 14

TABLE 18

Samples from the Fire Survey showing fluorescence at 254nm

Sample Number	Ref. Index	Colour of Fluorescence	Sides	Reaction with Cacotheline
9	1.5261	Amber	Both	None
51	1.5097	Blue	Both	None
100	1.5176	Green	One	Violet Colouration
123	1.5163	Blue	Both	None
198	1.5245	Yellow	One	None
280	1.5162	Violet	Both	None
307	1.5158	Violet	One	None
343	1.5158	Violet	One	None
377	1.5232	Green	Both	None
403	1.5262	Violet	One	None
421	1.5250	White	Both	None
571	1.5213	White	One	None
606	1.5160	Violet	Both	None
610	1.5283	Blue	One	None
698	1.5201	Blue	One	None
699	1.5299	Blue	One	None
701	1.5230	Green	Both	None
792	1.5162	Violet	Both	None
831	1.5241	White	Both	None
849	1.5307	Blue	One	None
927	1.5231	White	Both	None

EFFECT OF AGE OF BUILDING ON THE REFRACTIVE INDEX

DISTRIBUTION OF GLASS BROKEN IN FIRES IN ENGLAND AND WALES - 1 UP TO 1900 400 SAMPLES

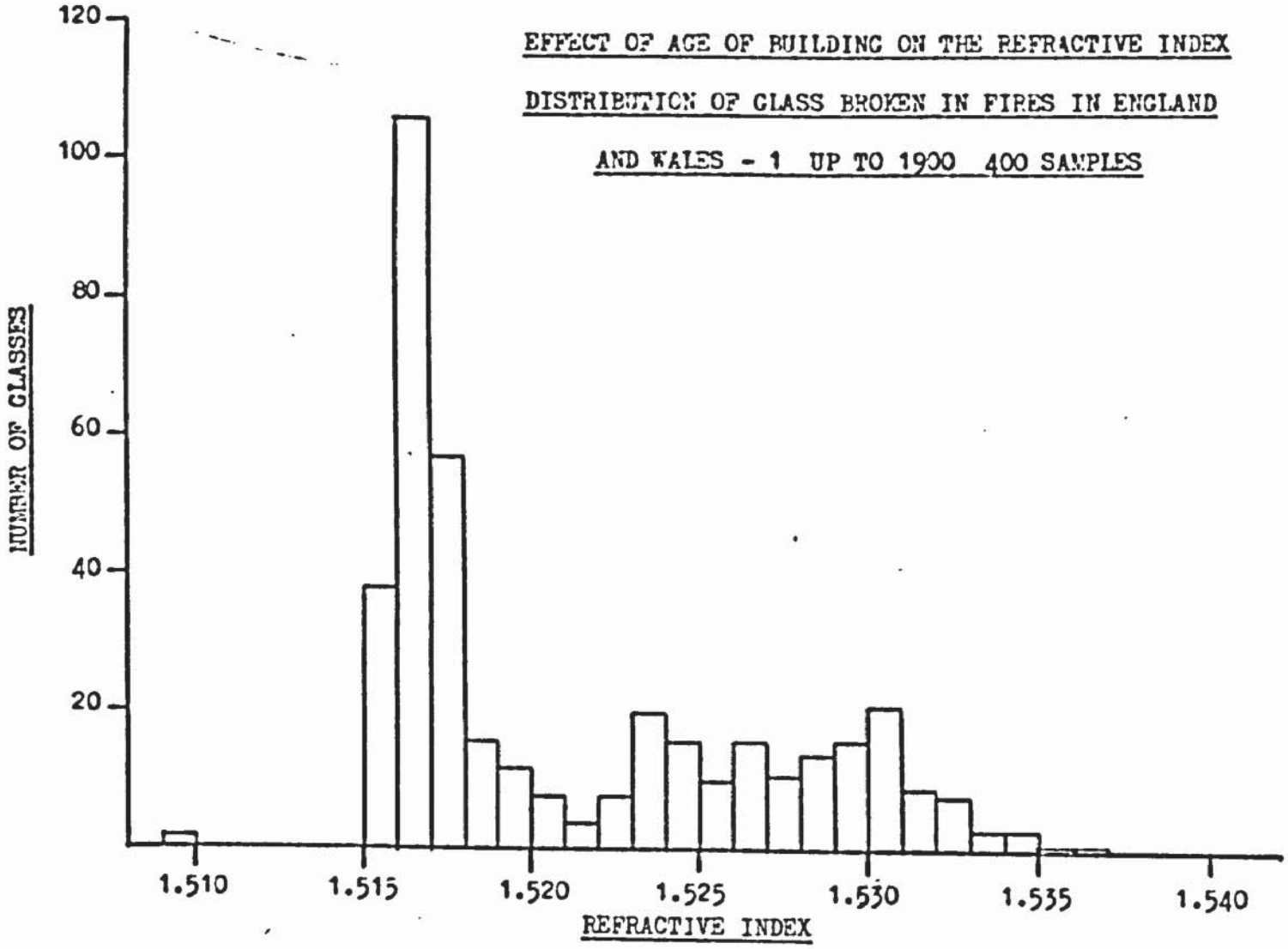


FIG. 15

EFFECT OF AGE OF BUILDING ON THE REFRACTIVE INDEX

DISTRIBUTION OF GLASS BROKEN IN FIRES IN ENGLAND

AND WALES - 2 1901-1944 263 SAMPLES

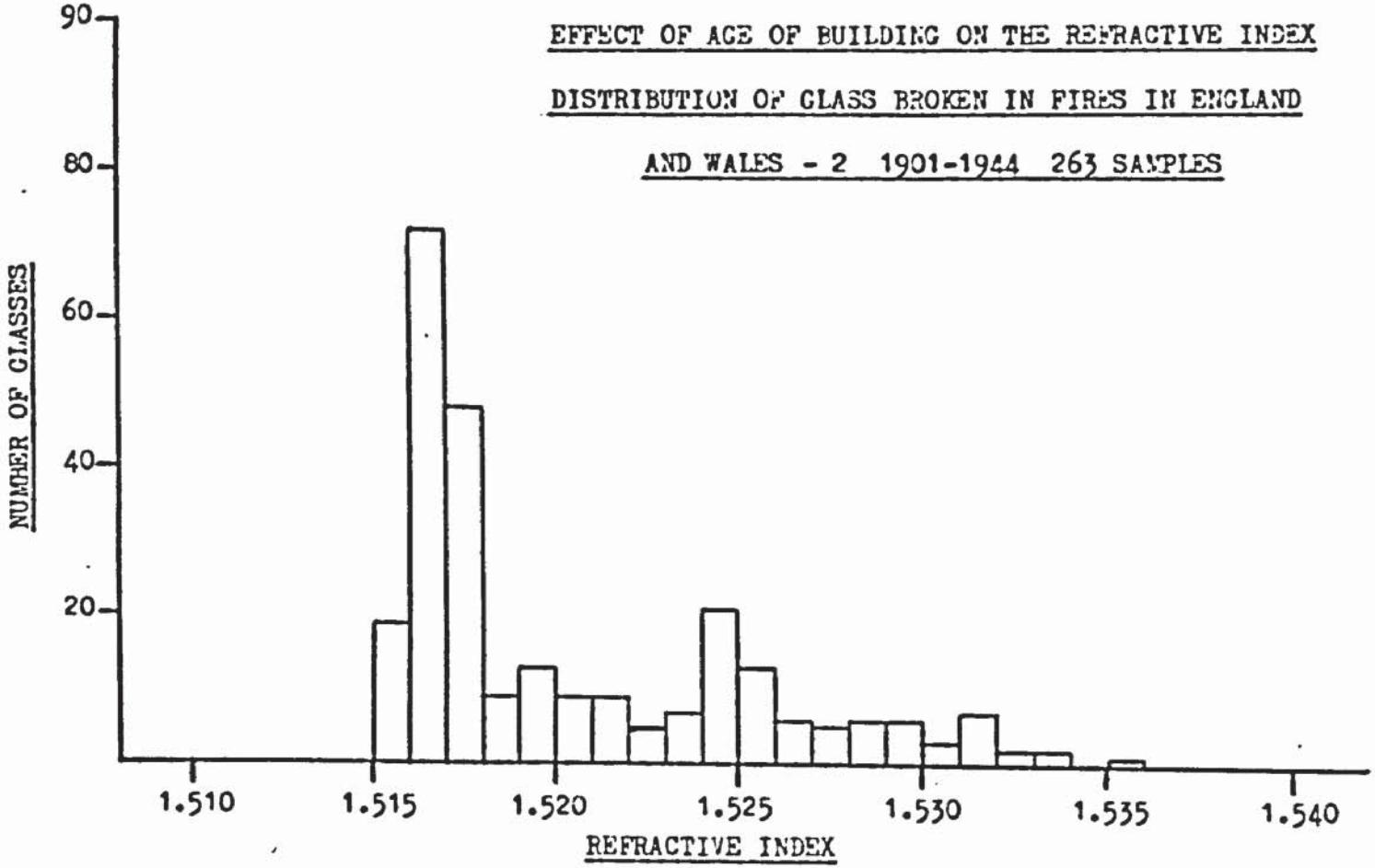


FIG. 16

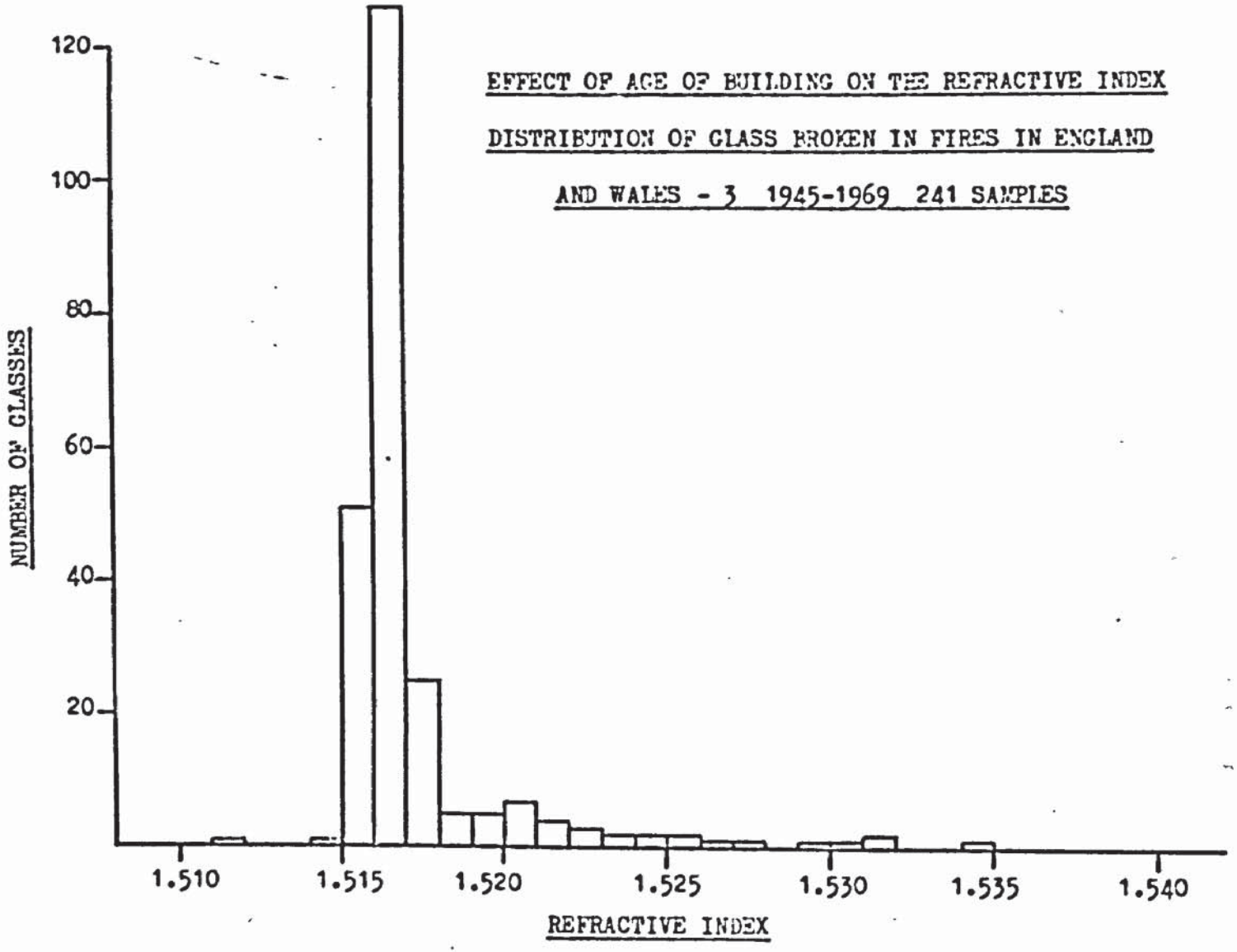

EFFECT OF AGE OF BUILDING ON THE REFRACTIVE INDEX
DISTRIBUTION OF GLASS BROKEN IN FIRES IN ENGLAND
AND WALES - 3 1945-1969 241 SAMPLES
NUMBER OF GLASSES
120
100
80
60
40
20
1.510
1.515
1.520
1.525
1.530
1.535
1.540
REFRACTIVE INDEX

FIG. 17

thirty-five cases the buildings were not classified for construction date.

The questionaire on the sample bags requested information on the type of buildings. Four hundred and sixty samples (49.0%) were received from private dwellings, 151 (16.1%) from factory premises, 20 (2.1%) from offices, 96 (10.2%) from shops, and 211 (22.5%) from other miscellaneous types of buildings.

In order to make valid statistical comparisons, samples from factory premises, offices and shops were grouped together. The combined refractive index distribution of samples from these three types of buildings was compared to the refractive index distribution of the entire survey using the χ^2 test. Similar tests were made for private dwellings against the entire survey and miscellaneous types against the entire survey. The following values of χ^2 where obtained:-

(1) private dwellings 21.0 (19 degrees of freedom)

(2) factories, offices and shops 19.3 (13 degrees of freedom)

(3) all other building types 18.6 (13 degrees of freedom)

In each case the value of χ^2 was less than the value obtained for the appropriate number of degrees of freedom obtained from tables[87] at the 10% level. Therefore, there is no evidence that any of the groups are different from the survey as a whole. A value of χ^2 as large as those obtained would be expected by chance in 10% of the cases examined.

The samples were divided into four groups according to the geographical location of the building from which the sample was taken. The division followed national and county boundaries.

Group 1 Hampshire, Surrey, Kent, Sussex, Middlesex, London, Essex, Hertfordshire, Bedfordshire, Berkshire, Buckinghamshire, Oxfordshire (320 samples).

Group 2 Suffolk, Huntingdonshire, Cambridgeshire, Norfolk, Northamptonshire, Leicestershire, Warwickshire, Worcestershire, Staffordshire, Cheshire, Nottinghamshire, Lincolnshire, Derbyshire (207 samples).

Group 3 All Wales, Shropshire, Herefordshire, Monmouthshire, Gloucestershire, Wiltshire, Somerset, Dorset, Devon, Cornwall (128 samples).

Group 4 Lancashire, Yorkshire and all northern counties (284 samples).

The refractive index distribution of each of these four groups was compared to the combined refractive index distribution using the χ^2 test. The following χ^2 values were obtained.

Group 1	20.3	(17 degrees of freedom)
" 2	10.3	(13 degrees of freedom)
" 3	8.9	(6 degrees of freedom)
" 4	15.3	(17 degrees of freedom)

In each case the value of χ^2 obtained was less than the value for the appropriate number of degrees of freedom obtained from tables[87] at the 10% level and, therefore, there is no evidence that any of the groups were different to the survey as a whole.

A χ^2 test comparing the number of the samples received from each of the 94 brigades (a total of 939) to the number requested (a total of 1272) gave a value of χ^2 of 65.8 (57 degrees of freedom). The value of χ^2 at the 10% level is 74.4

for 57 degrees of freedom and, therefore, there is no reason to believe that the samples received were not representative of the survey as originally planned.

6.1.2. Discussion

The fact that the refractive index distribution of the damaged samples whose refractive index was determined using the Mettler FP2 hot-stage was statistically similar to the distribution of those samples whose refractive index was determined using the Abbe refractometer shows that these samples should not be excluded from the survey.

Of the 939 samples examined, only one sample showed the presence of surface tin, that is surface fluorescence on one side only at 254nm and a violet colouration after treatment with hydrofluoric acid and cacotheline reagent. The fact that this fluorescence was detected on one side only suggests that this sample was produced by the 'float' process[88,89]. The amount of this float glass taken over England and Wales as a whole evidently accounts for only a small percentage of all window glass.

The comparison of the number of samples received from each brigade with the number of samples requested shows that this survey is no less representative than the survey as originally planned.

There is no evidence from this survey that the refractive index distribution is different in any of the four geographical groups considered when compared to the refractive index distribution shown in the survey taken as a whole. Although this similarity is to be expected for the respective density distribution, the information presented should not be extended to include similarity in chemical composition. Similarly, there is

no evidence from this survey that the refractive index distribution is different in any of the three building types namely, factories, offices and shops taken together as a group, private dwellings and other building types, when compared to the refractive index distribution of the survey taken as a whole.

The relationship between refractive index and density of samples in this survey will be discussed later.

6.2 SURVEY OF GLASSES FROM THE SCENES OF CRIME IN LIVERPOOL

6.2.1. Experimental

One hundred and eighty-four samples of broken window glass from the scenes of crime were collected by the Liverpool City Police over the period 1964 to 1968. Details of the premises from which the samples of glass were taken showed that 73 samples (39.7%) came from shops, 53 (28.8%) came from houses, 2 (1.1%) came from factories, 10 (5.4%) came from offices and 46 (25.0%) came from miscellaneous building types. The glass was cleaned in hot concentrated nitric acid, rinsed well with distilled water and dried on paper tissue. A piece of glass measuring approximately 10mm x 15mm was cut from each sample with a glass cutter and the refractive index of each piece measured on an Abbe refractometer (Section 4.1.1.). Thirty-one samples were unsuitable for measurement on the Abbe refractometer, i.e. patterned glass and glass with damaged surfaces and in these cases the refractive index was determined using the Mettler hot-stage (section 4.1.3.). One determination was made on each sample using a few milligrammes of crushed glass. A histogram of frequency vs refractive index for all the 184 samples is shown in Figure 18.

The thickness of each glass sample was measured to the nearest 0.05mm using a vernier caliper gauge. 165 samples were suitable for measurement and a histogram of frequency vs thickness is shown in Figure 19.

Each sample was examined under ultra-violet light of 254nm. Fifteen samples showed a white or pale-green fluorescence on one side only. On each of these samples the fluorescent side

REFRACTIVE INDEX DISTRIBUTION OF 184 GLASS SAMPLES
BROKEN BY CRIMINAL ACTIVITY IN LIVERPOOL

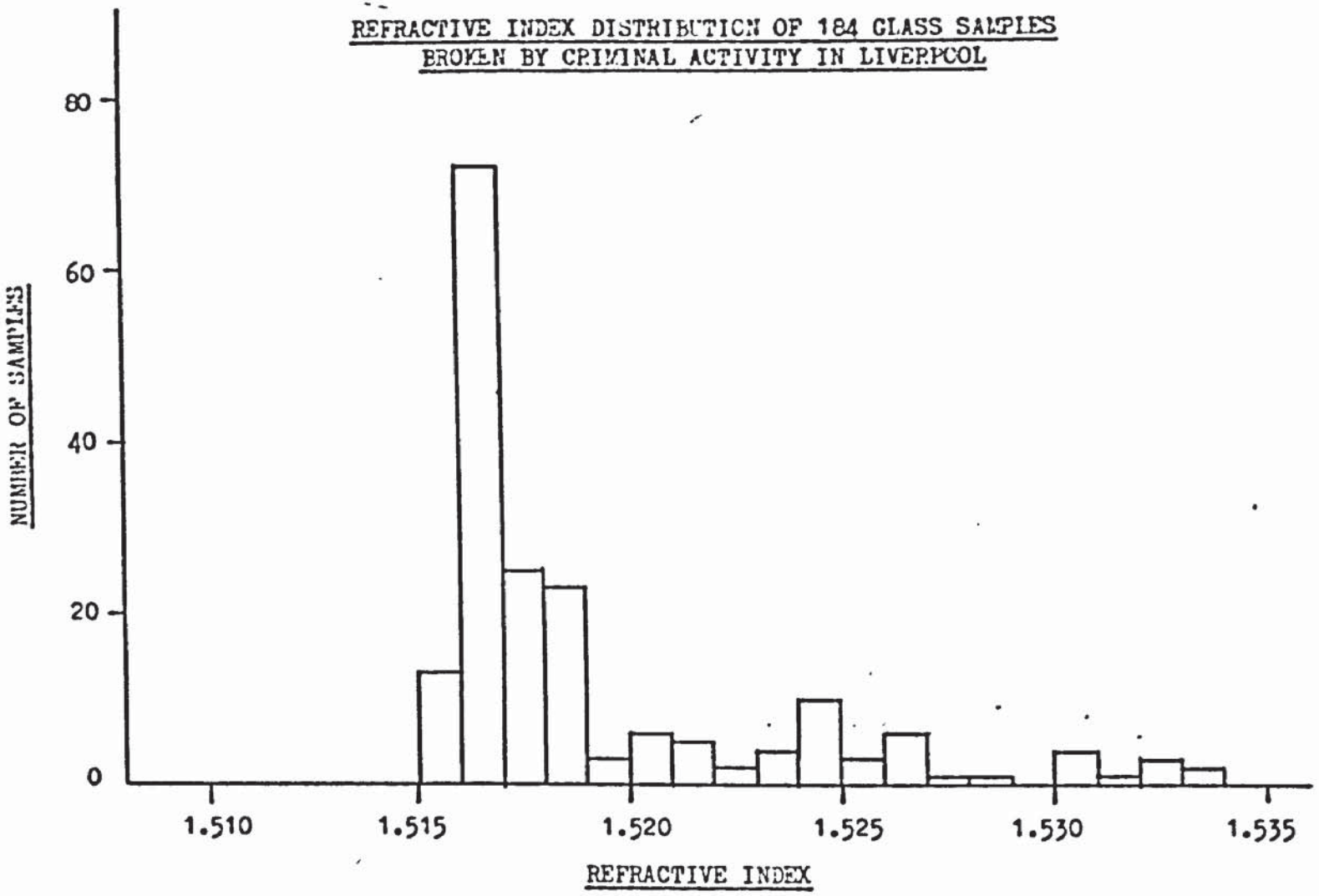


FIG. 18

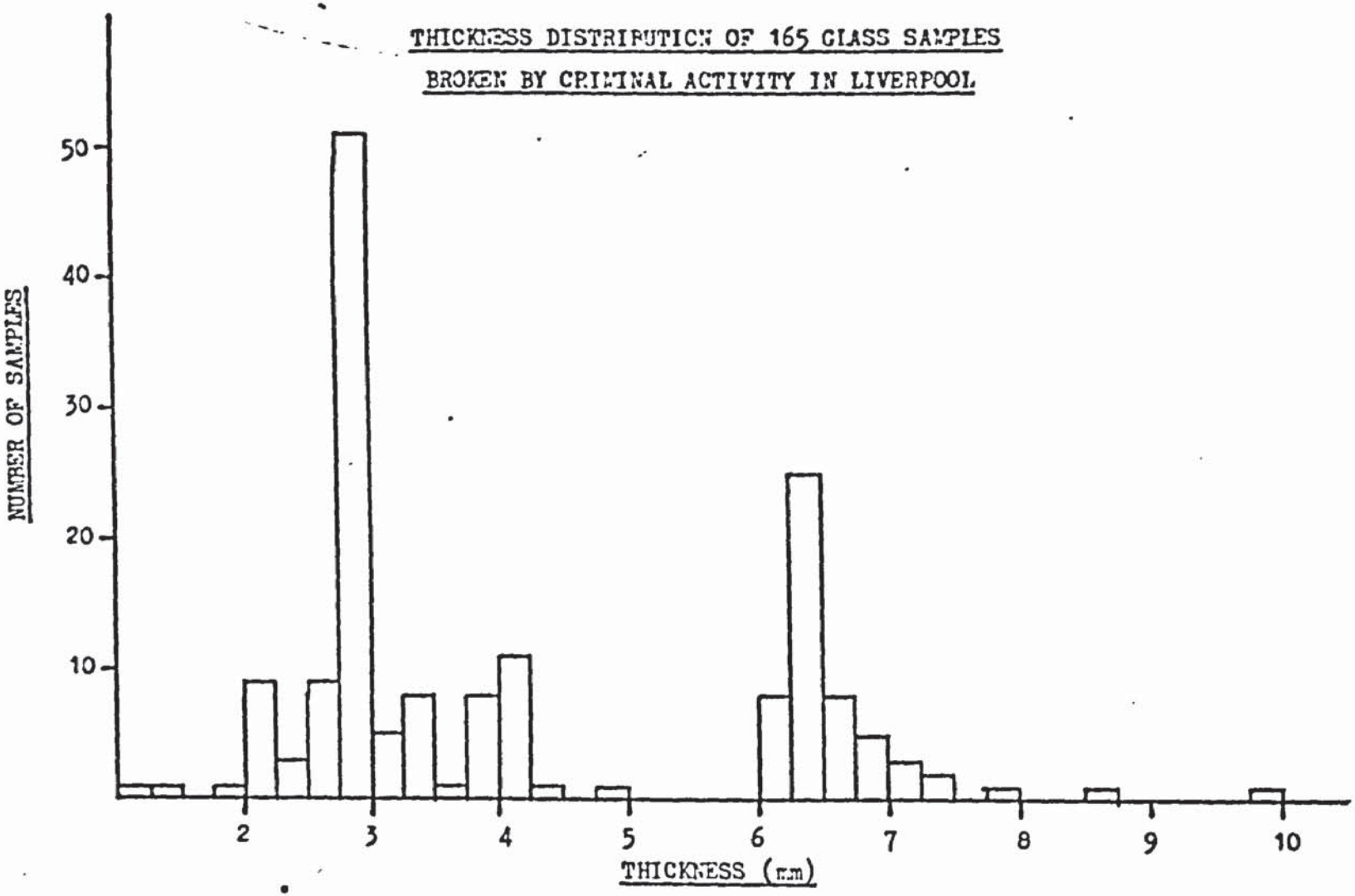

THICKNESS DISTRIBUTION OF 165 GLASS SAMPLES
BROKEN BY CRIMINAL ACTIVITY IN LIVERPOOL
NUMBER OF SAMPLES
50
40
30
20
10
2
3
4
5
6
7
8
9
10
THICKNESS (mm)

FIG. 19

was treated with 1 drop of 40% hydrofluoric acid followed by one drop of cacotheline reagent. In each case a purple colouration was obtained indicating the presence of tin. The results are shown in Table 19.

6.2.2. Discussion

The most remarkable feature of this survey was the large number of glasses which had traces of tin on one side (8.2%), indicating that they were manufactured by the float process. The refractive index of the samples having tin on one of their surfaces was 1.5180 $\pm$ .0005 and this explains the large amount of glass in the region 1.5180-1.5189. It would appear that any glass with a refractive index of 1.5180 $\pm$ .0005 and showing a white or pale-green fluorescence at 254nm could be classified as float glass.

TABLE 19

Samples from the Liverpool Survey showing Fluorescence at 254nm

Sample Number	Ref. Index	Colour of Fluorescence	Sides	Reaction with Cacotheline
4	1.5180	Pale Green	One	Violet Colouration
17	1.5177	White	One	Violet Colouration
33	1.5180	White	One	Violet Colouration
37	1.5180	Pale Green	One	Violet Colouration
38	1.5180	Pale Green	One	Violet Colouration
56	1.5180	Pale Green	One	Violet Colouration
57	1.5180	Pale Green	One	Violet Colouration
58	1.5181	Pale Green	One	Violet Colouration
63	1.5180	Pale Green	One	Violet Colouration
80	1.5179	Pale Green	One	Violet Colouration
85	1.5178	Pale Green	One	Violet Colouration
91	1.5179	Pale Green	One	Violet Colouration
92	1.5178	Pale Green	One	Violet Colouration
100	1.5180	Pale Green	One	Violet Colouration
182	1.5181	Pale Green	One	Violet Colouration

6.3 SURVEY OF GLASS FROM A DEMOLITION SITE AND A REFUSE TIP

6.3.1. Experimental

One hundred and ninety-two samples of glass were collected from a demolition site in Reading. The area was mainly residential involving houses between 80 and 100 years old and was being cleared for re-development. Glass was collected by breaking windows in downstairs rooms and taking one piece of glass from each broken pane. Samples were also collected from the ground on another part of the site. A further 181 samples of glass were collected from a Reading Council refuse tip which had been closed since 1950. The glass from the refuse tip was sampled by walking across the tip and picking up pieces randomly. Only one piece was taken from each 'pile' of glass to avoid collecting large quantities of glass which could have come from the same pane. In addition, the survey was confined to flat glass (of any colour), including mirror glass. Pieces of toughened windscreen glass and bottle glass, etc. were ignored.

All of the samples in each of the two groups of glasses were scrubbed in a strong solution of Teepol to remove the loose dirt and then rinsed in water. Approximately one gramme of glass was cut from each piece and the smaller pieces were given a further wash in 50% nitric acid followed by rinsing in distilled water. As might be expected, glasses removed from windows were much cleaner than glass which had been in the rubbish tip for 17 years. The samples were finally dried at 100°C. This procedure removed all the ferric stains from the glasses recovered from the rubbish tip.

The samples were placed in a solution of potassium mercuri-iodide contained in a stoppered 1 litre measuring cylinder, which in turn was contained in a constant temperature water bath at 25°C. Calculated amounts of water were added to reduce the specific gravity of the solution by fixed amounts (0.01). After each addition, the specific gravity of the solution was determined in triplicate using density bottles. All the samples which had sunk were then removed and counted. A histogram showing the frequency against specific gravity is shown in Figures 20 and 21.

6.3.2. Discussion

The method described provides a convenient method for determining the specific gravity distribution of a collection of glasses. It has the advantage that the time needed for the experiment is not dependent on the number of samples examined because the whole experiment may be conducted by weighing the number of samples which have sunk if the samples are too numerous to count.

In each of the two groups of glasses examined there is a considerable spread in the value of the specific gravity and, therefore, this would be a useful parameter in distinguishing between glasses. In addition, it is interesting to note that the peak with the higher specific gravity from the demolition site is somewhat narrower than the broad peak obtained from the refuse tip.

Both of the groups of glasses examined could be classified as having come from 'non-criminal' sources. However, they are clearly not representative of glass from the country as a whole and are, therefore, of limited value if considered in

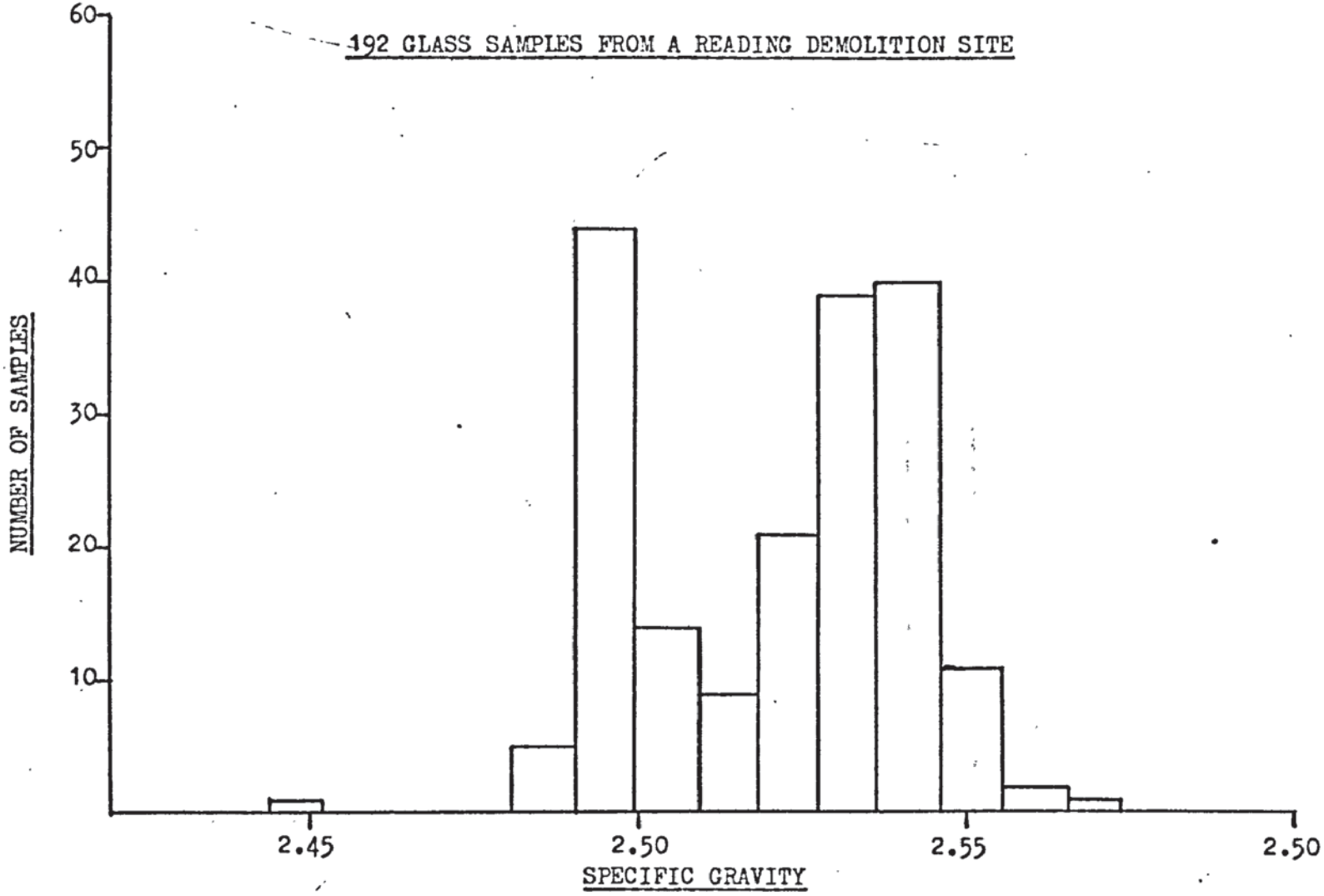

192 GLASS SAMPLES FROM A READING DEMOLITION SITE
NUMBER OF SAMPLES
60
50
40
30
20
10
2.45
2.50
2.55
2.50
SPECIFIC GRAVITY

FIG. 20

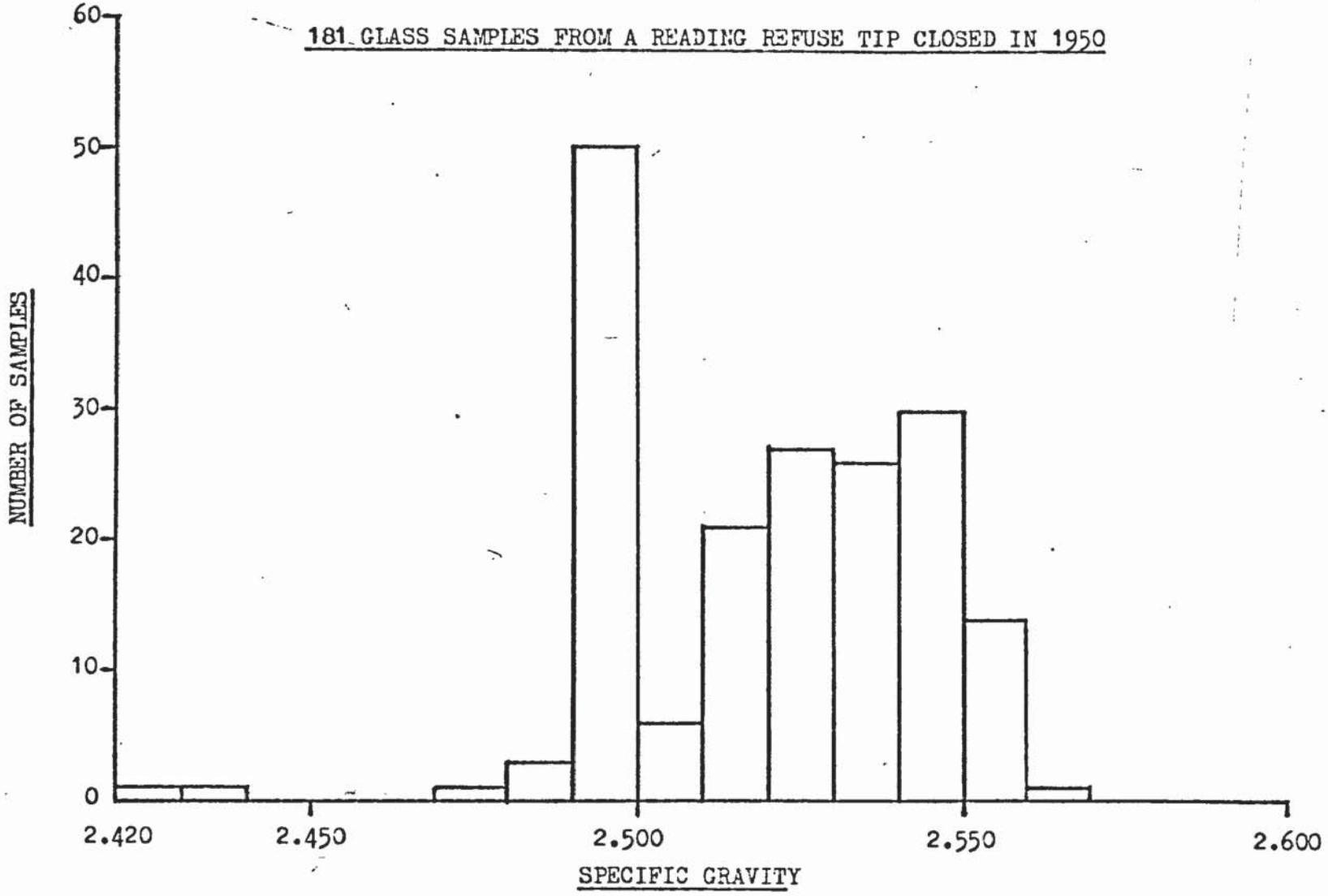

181 GLASS SAMPLES FROM A READING REFUSE TIP CLOSED IN 1950
NUMBER OF SAMPLES
60
50
40
30
20
10
0
2.420
2.450
2.500
2.550
2.600
SPECIFIC GRAVITY

FIG. 21

isolation. The two groups were examined early in the study to obtain information on the likely variation between different sampling methods and to test an experimental procedure for the examination of a large number of glass samples.

6.4 SURVEY OF GLASS ON CLOTHING

In the investigation of many crimes, fragments of glass are removed from clothing and after comparison with control samples, evidence is presented in court. There is, however, a complete absence of data relating to the relative frequency of occurrence of glass on clothing that is in no way related to crime.

A complete survey of glass on clothing would involve sweeping down a wide variety of garments from many people with consideration given to a number of variables such as age, sex, occupation and the geographical location of the people concerned. In addition, the fragmentary nature of glass recovered from clothing would make a comprehensive study of the physical and perhaps chemical properties of each fragment impossible. There would also be problems in defining exactly of what one sample consisted. For example, a man's trouser turn-ups may contain a large amount of glass of similar refractive index and density. This could be due to the fact that he had recently broken the windscreen on his car and, therefore, all the glass found should be treated as one sample or it could be that he was a glass merchant and the glass fragments found were, in fact, chips from many samples of glass and each should, therefore, be treated as a separate sample. Because of these difficulties, it was decided to carry out only a limited survey and examine men's jackets and trousers only. The suits were obtained from a single dry cleaning establishment in Reading. Obviously the survey could not be representative of the whole country, but it does provide an indication of the amount of glass found on clothing and also gives

some idea of the range of refractive index of the glass.

6.4.1. Experimental

(a) Sampling. Over a period of about three months during the middle of 1967, the dry cleaning establishment was visited almost daily and men's jackets and trousers which occurred together as a pair (but not necessarily matching) were chosen at random from the garments as they were delivered to the establishment. Altogether 100 pairs of jackets and trousers were examined, averaging about 2 pairs daily.

Each garment chosen for investigation was held over large clean brown paper sheets and the contents of the turn-ups and pockets brushed onto separate sheets using a tooth-brush. The debris from each pair of jacket and trousers was collected separately in three fractions:-

1. turn-ups
2. trouser pockets
3. jacket pockets

After collection each fraction was emptied into a labelled, previously inspected clean polythene container having a tight fitting snap-on lid.

Each of the three fractions of debris taken from the 100 pairs of jackets and trousers was emptied into a clean petri-dish and examined under a Nikon Zoom microscope. Incident light was used in the examination and the microscope was adjusted to give a magnification of X16. Fragments of interest were examined under higher magnification (up to X80) and then placed on a labelled microscope slide for further identification.

The lower limit of size of material taken from each debris fraction for further identification as glass was somewhat

subjective, but fragments which were much below 100µm were not considered. Above this limit all material which appeared to be glass was removed and stored separately for further identification. When the microscope slides containing the glass were not being examined they were covered with a cover-slip and sealed with sellotape.

For the purpose of this survey, glass is defined as transparent material which is isotropic in polarised light, is not indented by a dissecting needle and which is insoluble in acetone, concentrated nitric acid and water. Each fragment of glass-like material was examined separately and if it possessed the properties referred to, it was classified as glass.

(b) Examination. The refractive index of each fragment of glass was determined without crushing using the Becke line technique as described in section 4.1.3.

The largest dimension of each fragment was measured using a 'Projectina' projection microscope at X10 magnification. A stage graticule was used to calibrate the screen.

The colour of the glass fragments was determined subjectively under a microscope using a tungsten filament lamp as the source of illumination.

A total of 551 fragments of glass were found in the debris from 63 of the 100 suits examined. The remaining 37 suits did not contain glass fragments. Seventy of the suits possessed trouser turn-ups and in 28 of these, 78 glass fragments were found. Fourty-two suits had no glass in the trouser turn-ups. All the suits examined contained trouser pockets and 291 fragments of glass were found in the trouser pockets of 32 suits. The remaining trouser pockets did not contain glass. Every suit

had jacket pockets and 28 of them contained 182 pieces of glass. The remaining jacket pockets did not contain glass.

Two suits contained 46% of all the glass found, one of them containing 166 fragments. The distribution of glass among the 100 suits examined is shown in Figure 22.

The largest glass fragment found had a length of 7.1mm; 18 were longer than 1.0mm and 128 longer than 0.5mm. Figure 23 shows the size distribution of the 551 glass fragments.

The refractive index of 494 glass fragments was measured. The remaining 57 samples either gave poor Becke lines, proved too small for analysis or, in the case of some of the very small samples ($<100\mu m$), were lost during handling. The refractive index distribution of glass found in the 100 suits is shown in Figure 24. The refractive index distribution of glass found in the suit containing the largest amount of glass is shown in Figure 25.

The 100 suits contained 13 coloured fragments of glass of which there were 8 brown (7 in one suit), 2 blue, 2 yellow and 1 green. A large number of samples possessed a pale straw colour, but it was not practical to count them because of the uncertainty in defining which were definitely coloured and which were not.

6.4.2. Discussion

The results show that on average, approximately two men's suits out of every three sent for dry cleaning contain one or more glass fragments. In the case of suits in use, this represents an extreme situation since suits sent for dry cleaning probably contain a maximum amount of debris.

DISTRIBUTION OF FRAGMENTS OF GLASS AMONG 100 SUITS OF CLOTHING

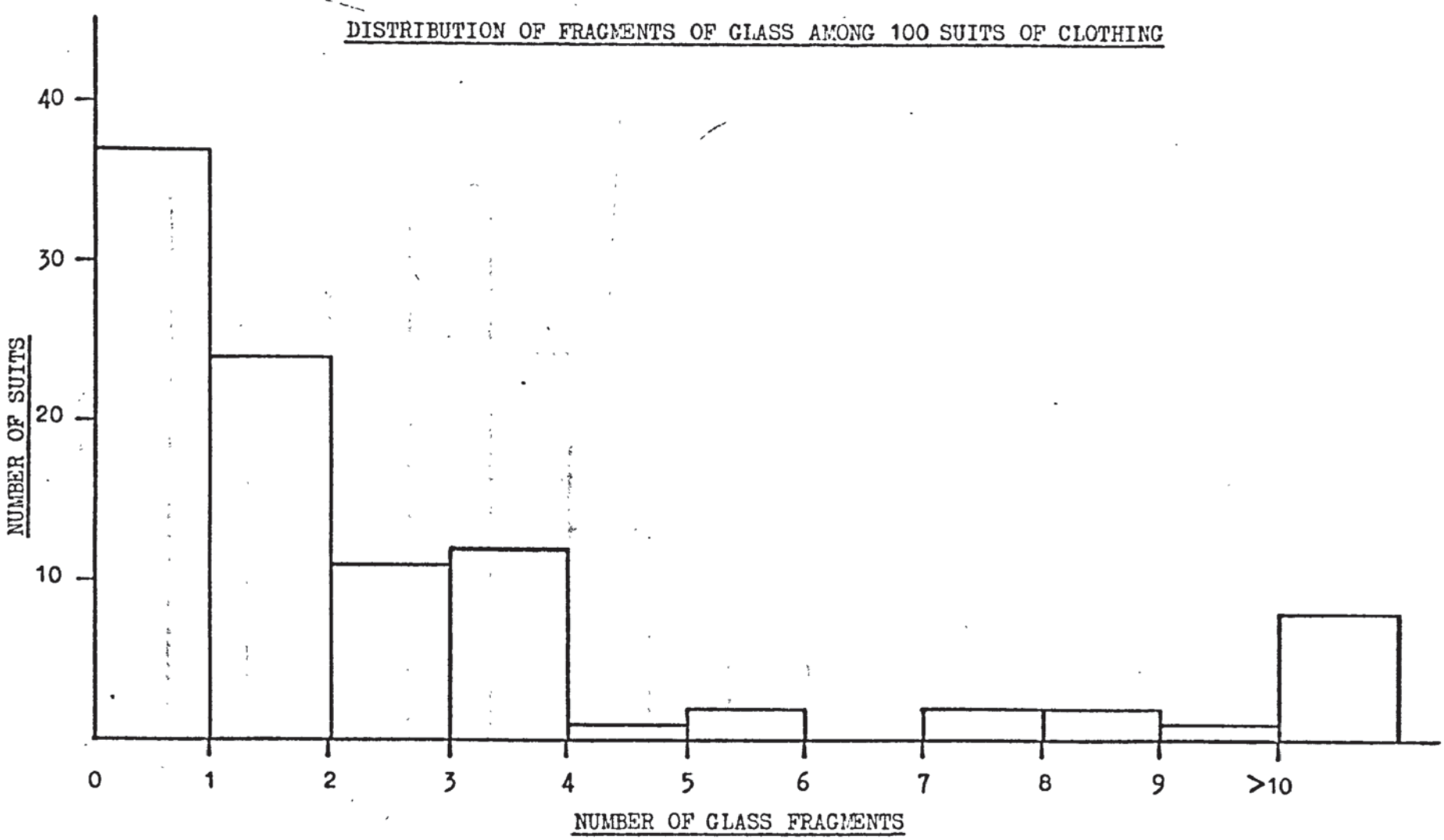


FIG. 22

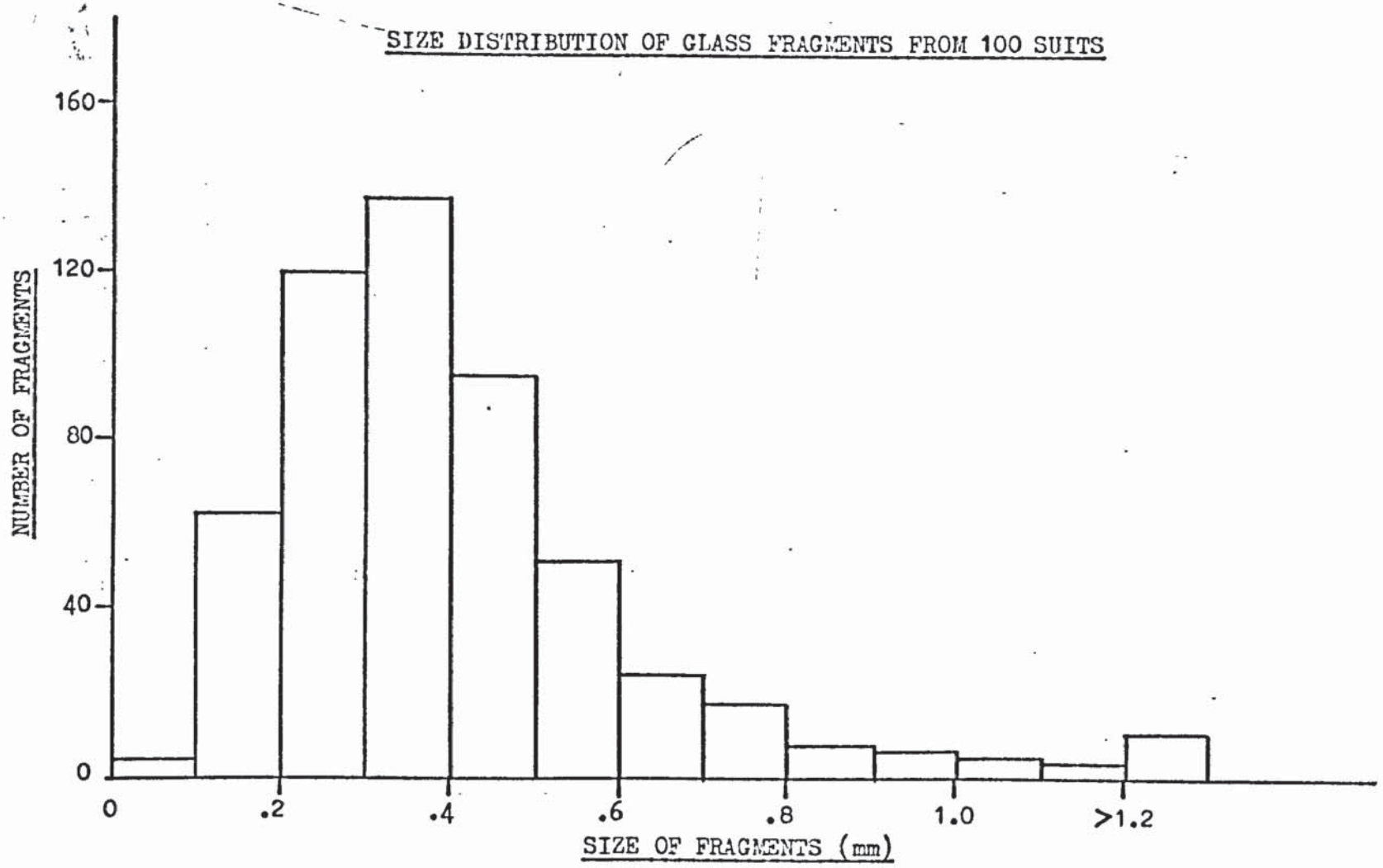

SIZE DISTRIBUTION OF GLASS FRAGMENTS FROM 100 SUITS
NUMBER OF FRAGMENTS
160
120
80
40
0
0
.2
.4
.6
.8
1.0
>1.2
SIZE OF FRAGMENTS (mm)

FIG. 23

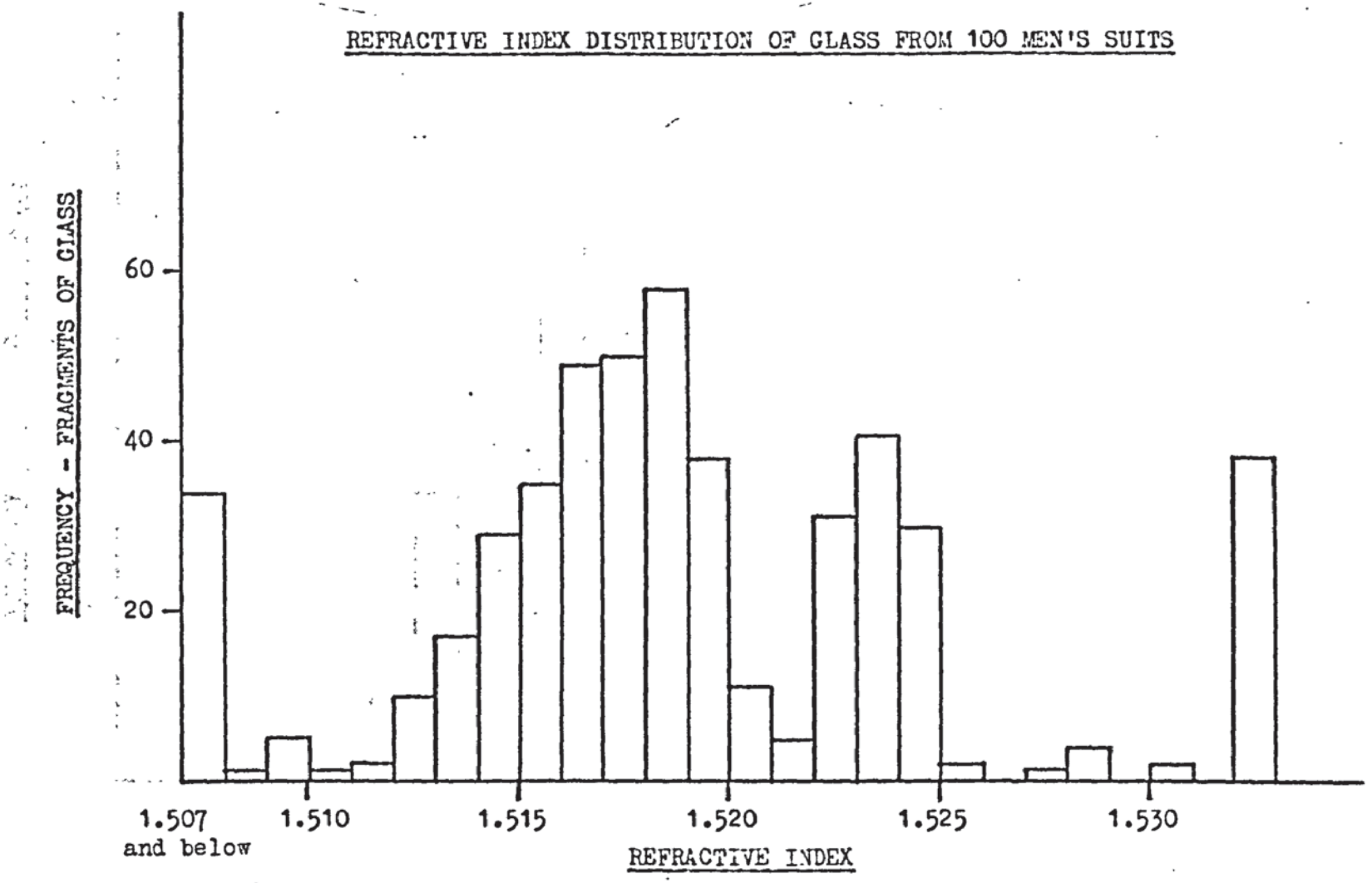

REFRACTIVE INDEX DISTRIBUTION OF GLASS FROM 100 MEN'S SUITS
FREQUENCY - FRAGMENTS OF GLASS
60
40
20
1.507
and below
1.510
1.515
1.520
1.525
1.530
REFRACTIVE INDEX

FIG. 24

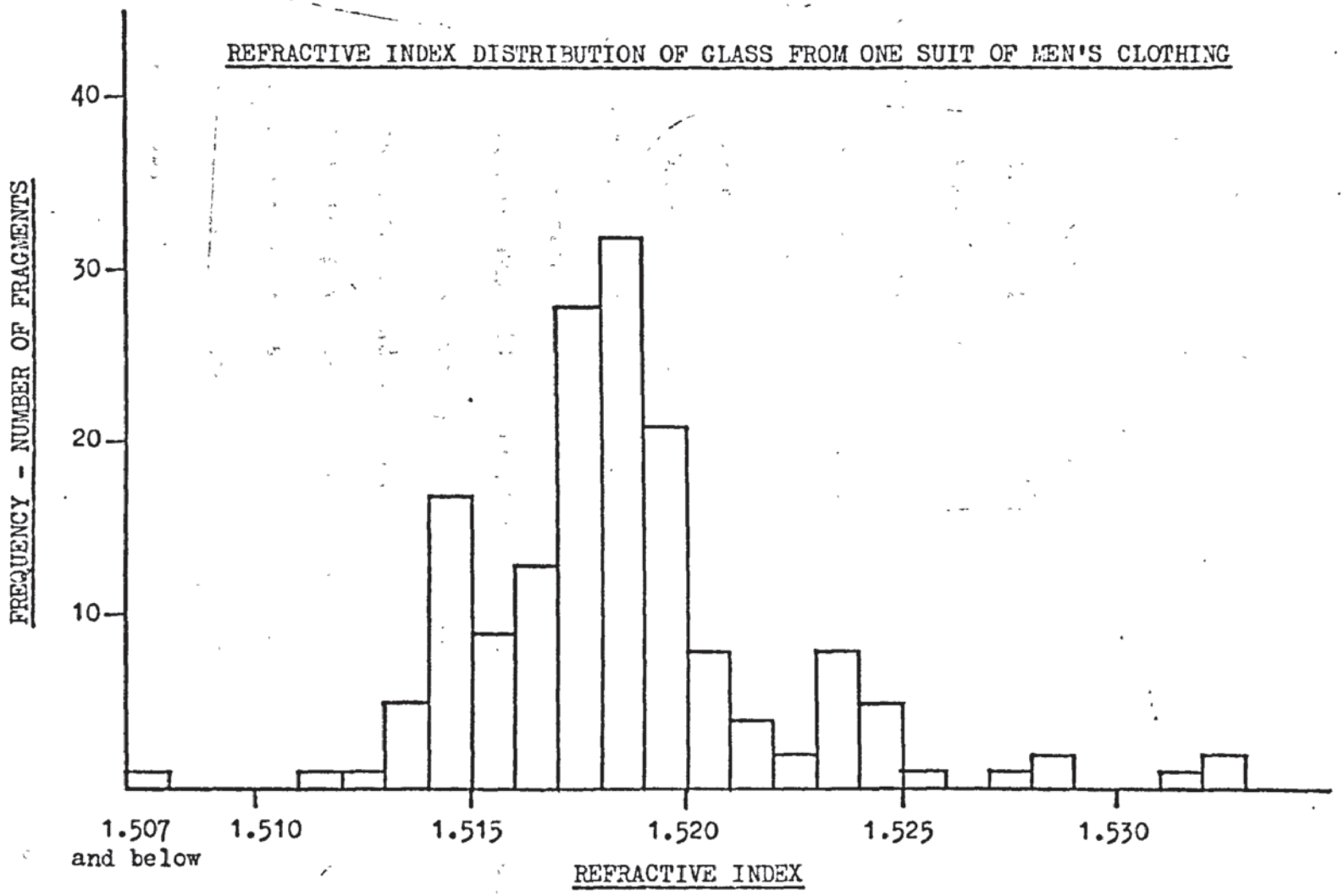

REFRACTIVE INDEX DISTRIBUTION OF GLASS FROM ONE SUIT OF MEN'S CLOTHING
FREQUENCY - NUMBER OF FRAGMENTS
40
30
20
10
1.507 and below
1.510
1.515
1.520
1.525
1.530
REFRACTIVE INDEX

FIG. 25

In a practical Forensic Science situation, fragments of glass weighing less than about 1mg or measuring less than about 1mm are not usually analysed unless there are special circumstances (e.g. a very large number of very small glass splinters being found covering the front of a jacket). In this survey only 18 fragments taken from 12 suits had a dimension greater than 1.0mm.

Thirteen fragments of glass were subjectively identified as being coloured, but in separate trials it was found impossible to classify reliably as coloured, fragments of glass which were known to have come from a dark brown beer bottle. The critical factor appeared to be the thickness because very thin fragments appeared virtually colourless. However, it is highly probable that many of the straw coloured glasses found in the survey originated from brown bottle glass.

The refractive index distribution of the fragments is interesting in that it is not similar to the published information on the refractive index distribution of window glass[30,80]. If it is assumed that all of the glass having a refractive index between 1.516 and 1.517 in Figure 24 is window glass, then reference to the other surveys mentioned above shows that approximately 30% of the glass in this survey is probably window glass. This estimate is likely to be in excess of the true figure, since it is unlikely that all the glass in the range 1.516-1.517 is window glass.

6.5 APPLICATION OF GLASS SURVEYS TO FORENSIC SCIENCE

The surveys considered above were all undertaken so that the results obtained could be used for Forensic purposes. In addition, various other workers[31,80,90] have undertaken similar surveys and it is interesting to compare these surveys with each other.

All the reported window glass distributions known to the author fall into two groups. The first group consists of distributions of the type published by Mullen[31] and Dabbs[81]. These surveys show a bimodal distribution, one peak corresponding to modern window glass and the other occurring at a specific gravity about 0.03 higher. The second group consisting of the remaining surveys studied is similar, except that the second peak is much smaller or entirely absent. A χ^2 test of Mullen's distribution (Figure 26) against the distribution obtained from a refuse tip by Dabbs (Figure 21) shows that although the two distributions appear similar, they are not statistically similar.

A paper by Cobb[80] describes a survey of glasses collected from the scenes of crime in the Birmingham area and shows a much smaller number of samples in the higher refractive index peak than is shown in Mullen's survey. Both these surveys cover a relatively small number of samples, but illustrate the differences which may occur between localized geographical regions (cf Fire Survey).

The Fire Survey (Section 6.1) is the largest single survey of the refractive index of window glass available at the time of writing and it is, therefore, worth comparing the other smaller surveys to it.

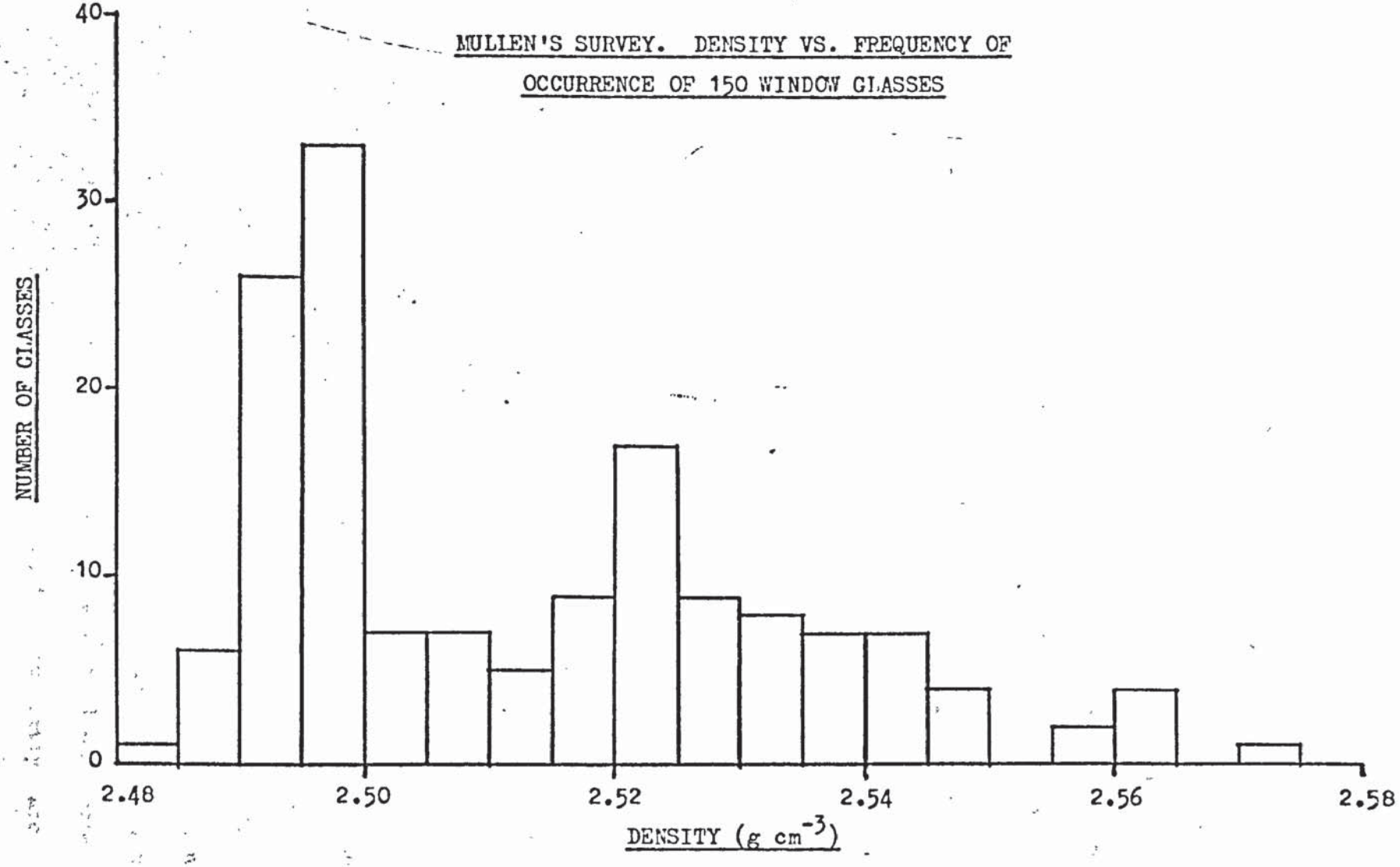

MULIEN'S SURVEY. DENSITY VS. FREQUENCY OF
OCCURRENCE OF 150 WINDOW GLASSES
NUMBER OF GLASSES
40
30
20
10
0
2.48
2.50
2.52
2.54
2.56
2.58
DENSITY (g cm^{-3})

FIG. 26

The Liverpool Crime survey collected at the same time as the Fire Survey shows some interesting differences. In the refractive index range 1.5180-1.5189, a greater proportion of samples were found in the Liverpool survey than in the Fire Survey. Whilst some of the difference may have been due to the effect of small sample size, the presence of float glass and the large number of shops in the Liverpool survey undoubtedly influenced the result. In the Liverpool Survey 15 samples (8.2%) were shown to be manufactured by the float process. In the Fire Survey only 21 samples (2.2%) showed any fluorescence at all and of these, only 1 (0.1%) was shown to be manufactured by the float process. A possible explanation for this is that as Liverpool is so near to Pilkington's factories, it may be receiving a larger proportion of float glass than the rest of the country. A χ^2 test of the Fire Survey (expected) against the Liverpool Crime Survey (observed) yielded a χ^2 of 66.5 for 11 degrees of freedom. If the two surveys were in fact similar, the numerical differences between them would be small and hence χ^2 would tend to zero. As the difference between the two surveys increases χ^2 will increase and tables have been published showing how high χ^2 may go before it becomes too high to be just 'bad luck'. In this case, when there are 11 degrees of freedom, χ^2 would be expected to exceed 19.7 only once in twenty trials if the two surveys were similar and to exceed 31.3, only once in 1,000 trials. It is conventional to express these chances as significance levels in percent, i.e. 1 in 1,000 would be 0.1%. The value of χ^2 obtained was 66.5 and it has already been stated that χ^2 will only exceed 31.3 once in 1,000 trials and, therefore, the two surveys are

significantly different. A succinct way of expressing this is that "the difference is significant at the 0.1% level".

A further interesting difference between these two surveys is in the thickness distributions. The Fire Survey shows only a small amount of glass (8%) with a thickness greater than 6.0mm, while the Liverpool survey shows considerable amounts (33%) of this type of glass. However, this is almost certainly due to the fact that in the Liverpool survey 39.7% of the samples came from shop premises compared with 10.2% in the Fire survey. (Shop windows are often glazed with a glass at least a quarter of an inch (6.35mm) thick). In addition, large differences were found in the percentage of samples from houses and factories in the two surveys.

The survey conducted at the Metropolitan Police Laboratory[90] (Figure 27) shows a very broad peak around the modern glass region compared to the Fire Survey. In addition, the sudden rise in the number of glasses in the region 1.531-1.534 is unusual and difficult to explain. A χ^2 test against the Fire Survey yielded a χ^2 of 68.1 for 11 degrees of freedom which shows a significant difference at the 0.1% level.

The survey published by Cobb[80] (Figure 28) looks somewhat similar to the Fire Survey, but the numbers of samples obtained with a refractive index over 1.527 is small. In addition, Cobb's survey contains more samples around a refractive index of 1.5200. This may be due to the relatively small sample size (175) or it may reflect the true situation. Chance-Pilkington have a factory in the West Midlands which produces patterned rolled sheet with a refractive index of approximately

REFRACTIVE INDEX DISTRIBUTION OF 178 GLASS SAMPLES FROM THE METROPOLITAN POLICE LABORATORY SURVEY[90]

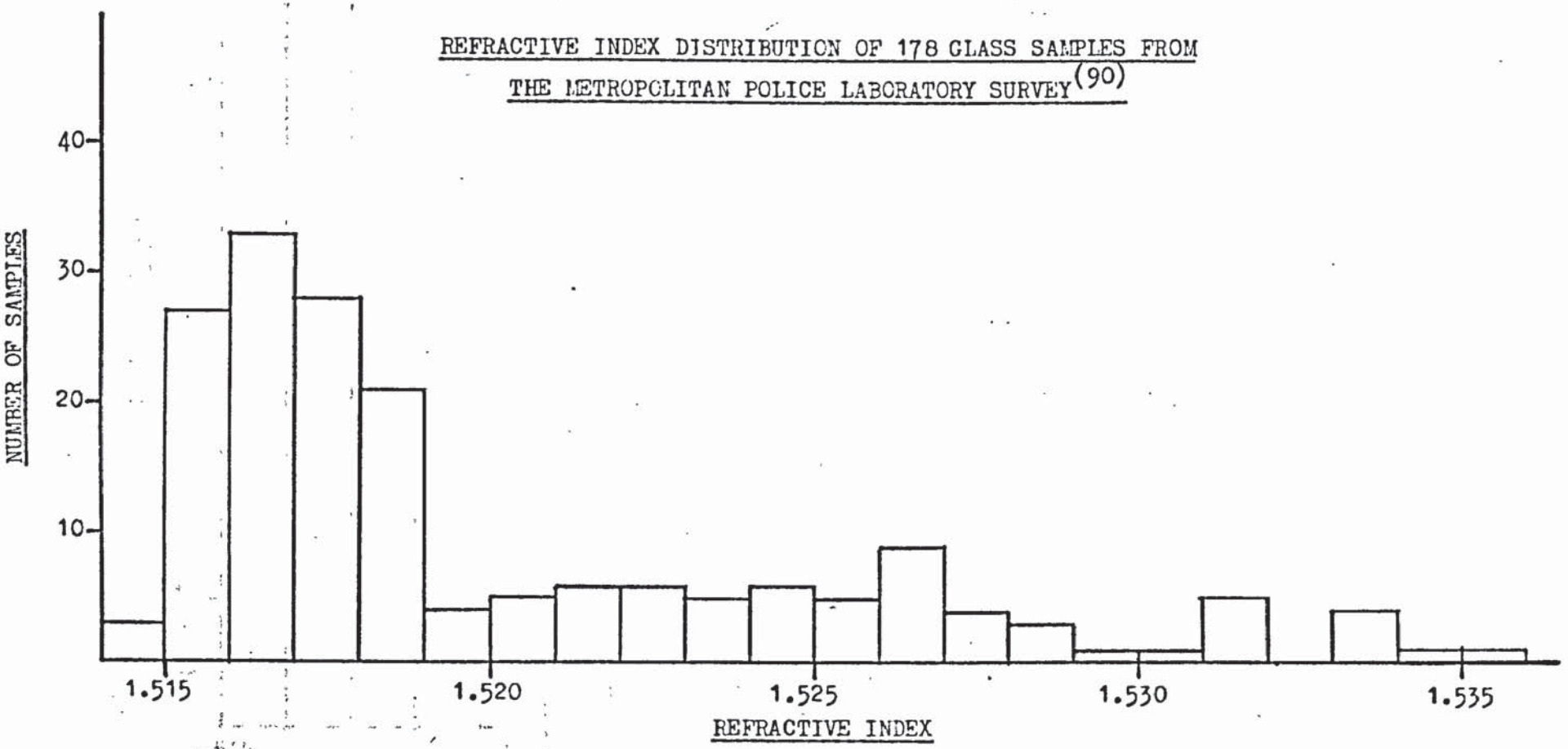


FIG. 27

COBB'S[80] SURVEY. FREQUENCY DISTRIBUTION OF REFRACTIVE INDEX OF 175 GLASS SAMPLES

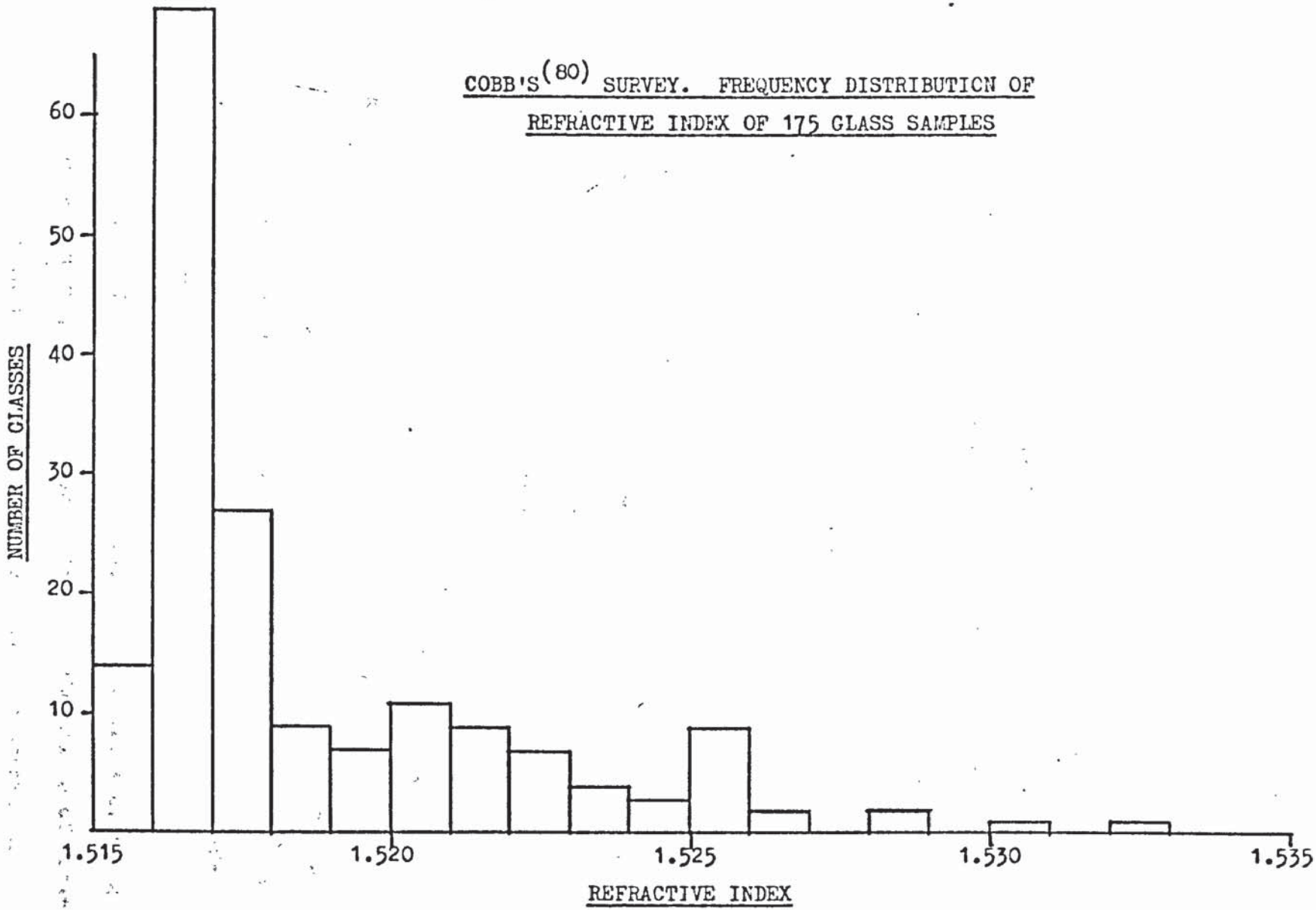


FIG. 28

1.524. A χ^2 test against the Fire Survey gave a χ^2 of 42.2 for 10 degrees of freedom which shows a significant difference at the 0.1% level.

Examination of Figures 12, 20 and 21 show that the smaller peak from the demolition site samples is less pronounced than the one from the rubbish tip samples and has virtually disappeared from distributions sampled at a later date. This illustrates the fact that surveys containing considerable amounts of older glass tend to give bimodal distributions in contrast to surveys containing a high proportion of modern glass, e.g. the Fire Survey, which tend to be unimodal. In addition, Figures 15-17 show the effect of the age of buildings, but these distributions are obviously affected to a certain extent by the replacement of broken windows, thereby introducing a greater amount of glass in the region 1.516. However, the essential point is that the glass population in England and Wales is changing with time and this factor should be taken into account when using a survey.

None of the glass distributions examined appear to be statistically similar to each other. Examination of the distributions show that in each case, the main peak occurs at the same refractive index and, therefore, calibration differences between the refractometers are unlikely to explain the observed differences.

Having found a fragment of glass on a suspects clothing the most pertinent question to ask is "What is the chance of finding a glass of this particular refractive index and density on clothing chosen at random". This question could be answered by

making a survey of clothing from all over the country, but it was shown in Section 6.4 that from 100 suits of clothing examined, there were only 18 fragments of glass taken from 12 suits of a size that would normally be examined in Forensic Science Laboratories. Therefore, it would be necessary to examine the debris from at least 10,000 suits in order to obtain a reasonable sample. Clearly this is not a practical proposition. If the suits were examined at a rate as high as 10 suits a week, the work would take 20 years to complete.

When dealing with samples as large as 1mg, it is fairly easy to identify coloured glass under a microscope. Therefore, in many cases it will be possible to distinguish coloured container glass from colourless types. In addition, future developments in the analysis of glass and in analytical techniques may make it possible to distinguish positively flat glass from other types. Under these circumstances, a survey of flat glass becomes an attractive alternative to the clothing survey.

Clearly, not all the surveys examined are equally useful for predicting the probability of occurrence of glass, although they all provide essential background information. The refuse tip survey was known not to contain any glass manufactured after 1952 and is, therefore, unsuitable in this case. Similarly, the demolition site survey only included glass from old houses over an extremely limited area and, therefore, this survey is also unsuitable. The three surveys carried out by Regional Forensic Science Laboratories (i.e. Cobb's survey, Mullen's survey and the Metropolitan Police Laboratory survey) contained less than 200 samples in each case, which is a relatively small

sample when compared to the amount of flat glass in use at the present time. In addition, the surveys covered only a small area of the country in each case and it cannot be assumed that these areas are representative of the country as a whole. Also Mullen's survey was carried out some time ago (1964-1967) and the distribution of glasses may have changed since then. A nation-wide survey of glasses broken in the course of criminal activity may prove to be a suitable population to work from and could prove to be similar to the Fire Survey. Such a survey would have the disadvantage that the basic survey was made on samples that were collected exclusively from the scenes of crime. However, it is known that, for various reasons, criminals repeatedly attack certain particular buildings and in certain circumstances, the same windows are broken repeatedly. In this case, if a survey was taken of glass broken at the scenes of crime, the distribution could well be biased in favour of modern glass. Taking all factors into account, it is probably better to avoid the use of crime surveys until more representative sampling surveys have been carried out.

The clothing survey is clearly unsuitable for consideration because of the small number of reasonably sized samples and the small geographical area over which the survey was carried out.

In contrast to all the other surveys, the Fire Survey has the advantage that it is a random nationwide survey of window glass which is unconnected with crime. Also it is the largest survey available.

This type of survey does have some disadvantages. Examination of the distributions obtained in the Fire Survey and the Clothing Survey show that they are markedly different in places. However, the positive identification of container glass or at least some of it, would reduce this problem.

A totally different approach would be to make a survey of broken glass as suggested by Page(84). A number of requests could be sent to a random selection of the population asking for a sample of the next glass article that they actually broke themselves. If the response was satisfactory, this would certainly produce a survey of broken glass in the country. However, the relationship between a survey of this sort and the clothing survey is difficult to predict. For example, a man sustaining a broken windscreen in his car is far more likely to get large quantities of broken glass on his clothing than if he broke a tumbler or dropped a mirror.

In conclusion, it can be said that the collection of a suitable number of glasses from which to estimate the probability of glass on clothing is a far from easy task. There are good reasons at the moment for choosing the Fire Survey as the parent population, but this does not exclude the use of other surveys in the future.

7. THE RELATIONSHIP BETWEEN REFRACTIVE INDEX AND DENSITY

The correlation between the refractive index and density of simple substances is well known and is discussed in many standard test books on physical chemistry. Glass is not a simple substance and commercial glasses often consist of a mixture of five or more oxides. Many workers[30,31,49,50,79,80] have reported a correlation between the refractive index and density of glasses, but several have shown that 100% correlation was not obtained in their studies and that some points lay a considerable distance from the best straight line through the remainder of the points. This could be due to a variety of reasons and clearly needs investigating.

The investigation was divided into two parts. In the first part a limited number of glasses were selected whose refractive index and density lay within the range of the samples commonly encountered in Forensic Science. The measurements of both parameters were made on the same piece of glass to avoid any possibility of variation in the physical properties due to heterogeneity that might occur if two separate samples were taken. In addition, the errors involved in the measurements were carefully determined to see if any deviation from linearity could be due to errors of measurement.

The second part of the investigation involved measuring the correlation between refractive index and density of the samples collected in the Fire Survey in order to establish the correlation coefficient for a large number of glasses which will be used to predict the frequency of occurrence of glass with known physical properties (Section 8).

7.1 EXPERIMENTAL

Thirteen samples of window glass 10mm x 15mm in the refractive index range 1.516-1.532 were selected and the refractive index determined on an Abbe refractometer, as described in Section 4.1.1.

The density was determined using the same samples that were used to measure the refractive index. The sink/float method was used, as described in Section 3.1.1. and the B.G.I.R.A. standards were used to obtain an absolute result. At least four determinations were made on each sample.

A plot of refractive index vs. density for the 13 samples is shown in Figure 29.

PLOT OF REFRACTIVE INDEX AGAINST DENSITY FOR 13 GLASS SAMPLES

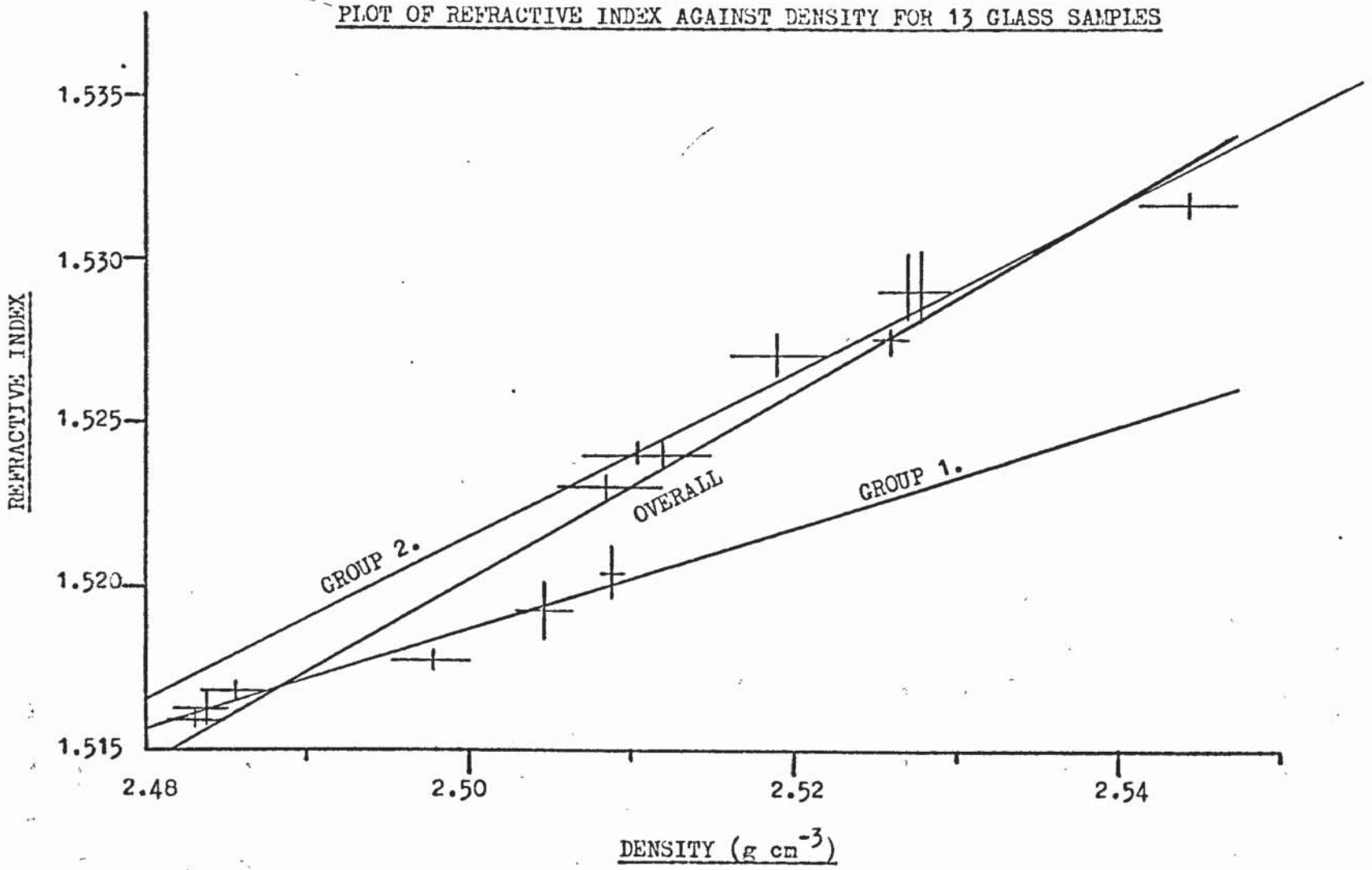


FIG. 29

7.2 DISCUSSION

The experiment was designed to determine if the scatter observed by several workers[30,31,80] when refractive index is plotted against density could be explained by the variation in physical properties between the separate samples used to determine the refractive index and the density (i.e. the variation over the pane), by the error associated with these measurements, or by some other factor. Any possible sample variation is eliminated by using the same samples for both refractive index and density and the limits of the errors ($\pm$ 3 standard deviations) are shown by the extended crosses in Figure 29. Because it is impossible to draw a straight line through all the points, even taking the errors into account, it may be concluded that there is a significant deviation from a straight line which is not due to either heterogeneity or experimental error and which may be of use in distinguishing glass samples.

The overall correlation coefficient was determined to be 0.96, but from Figure 29 it is clear that it is possible to divide the glasses into two groups and the best straight line (using the method of least squares) through each of the two groups is shown. The angle between the slopes of the two lines is .06458 radians (3.7°).

The Fire Survey

The correlation coefficient between density and refractive index for 338 Fire Survey samples was found to be 0.93. A graph of density vs. refractive index for 100 of these samples is shown in Figure 30. The number was restricted to 100 to avoid overcrowding. It is possible to divide the samples into two groups; those samples with a refractive index less than 1.519

PLOT OF DENSITY AGAINST REFRACTIVE INDEX FOR

100 SAMPLES OF GLASS FROM THE FIRE SURVEY

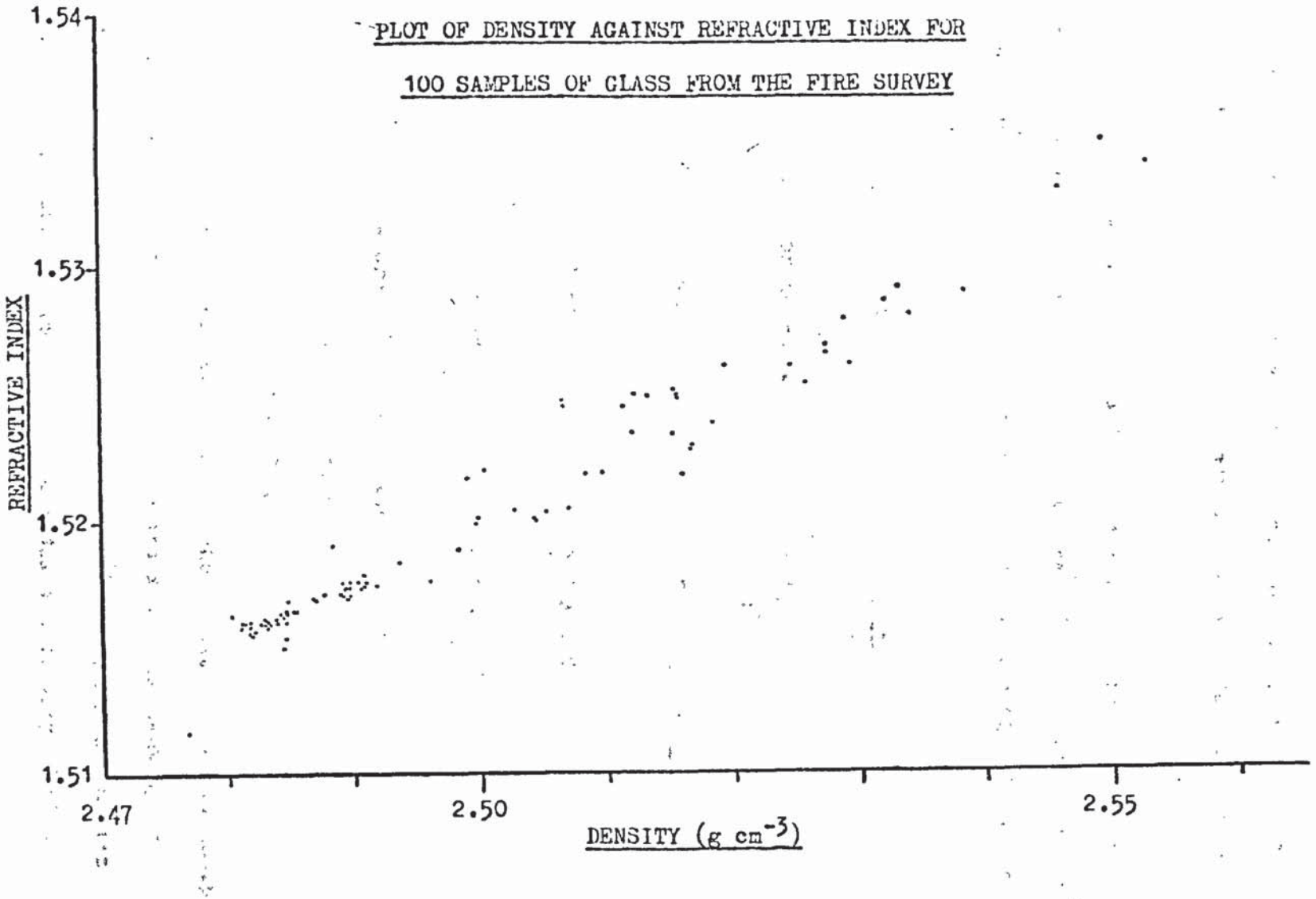


FIG. 30

(density $\simeq$ 2.50) and those with a refractive index above this figure. Reference to Figures 12, 18, 20, 21 and 26 in Section 6 shows that there is a trough in the histograms at this refractive index which separates modern production glass from the older glass which has a higher refractive index. The slight change in the slope at a refractive index of 1.519 on a plot of refractive index vs. density is almost certainly due to a change in the composition of the glasses.

There are several well known equations relating refractive index and density and several papers[49,50,79] have been published which consider these relationships. The equations considered are:-

1. Gladstone-Dale $$k = \frac{n - 1}{d}$$

2. Lorentz-Lorenz $$k = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

3. Eykman $$k = \frac{n^2 - 1}{n^2 + 0.4} \cdot \frac{1}{d}$$

4. Lichtenecker $$k = \frac{\log n}{d}$$

5. Newton-Drude $$k = \frac{n^2 - 1}{d}$$

where k = constant

n = refractive index

d = density

Inspection of each equation shows that the relationship between a function of the refractive index and the density is linear. However, several workers[30,31,80] have shown that the relationship between the refractive index and density of glass is

not always exactly linear and although the overall trend is to a linear relationship, some points lie a considerable distance from the best straight line through the points. This work confirms the observations of the other workers mentioned above and has shown that the deviation from linearity is not caused by measurement error or the effect of heterogeneity. As glass is a multi-component mixture, deviation from linearity is not surprising as there are many ways in which the components may be altered.

The constant k was calculated using the Lorentz-Lorenz equation for the 338 Fire Survey samples and a histogram of frequency vs. k (specific refractivity) is shown in Figure 31. Because the shape of the histogram is somewhat unusual, the 338 samples were divided into two mutually exclusive groups; one being all glasses in the refractive index range 1.514-1.519 and the other consisting of the remaining glasses. The resulting histograms are shown in Figures 32 and 33. The mean value of specific refractivity for glasses within the range 1.514-1.519 was found to be 0.121640 with a standard deviation of 0.000083. For glasses outside this range, the mean value was 0.121653 with a standard deviation of 0.000243.

The two distributions were tested for normality using the χ^2 test[98] and the values of χ^2 obtained are tabulated in Tables 20 and 21. Table 21 shows that the distribution in Figure 33 approximates to a normal distribution because the value of χ^2 is less than 16.92 which is the value of χ^2 at the 5% level. The distribution shown in Figure 32 is not normal. Examination of Table 20 shows that this is because there are too

HISTOGRAM OF FREQUENCY VS. SPECIFIC REFRACTIVITY (k)

OF 337 GLASS SAMPLES FROM THE FIRE SURVEY

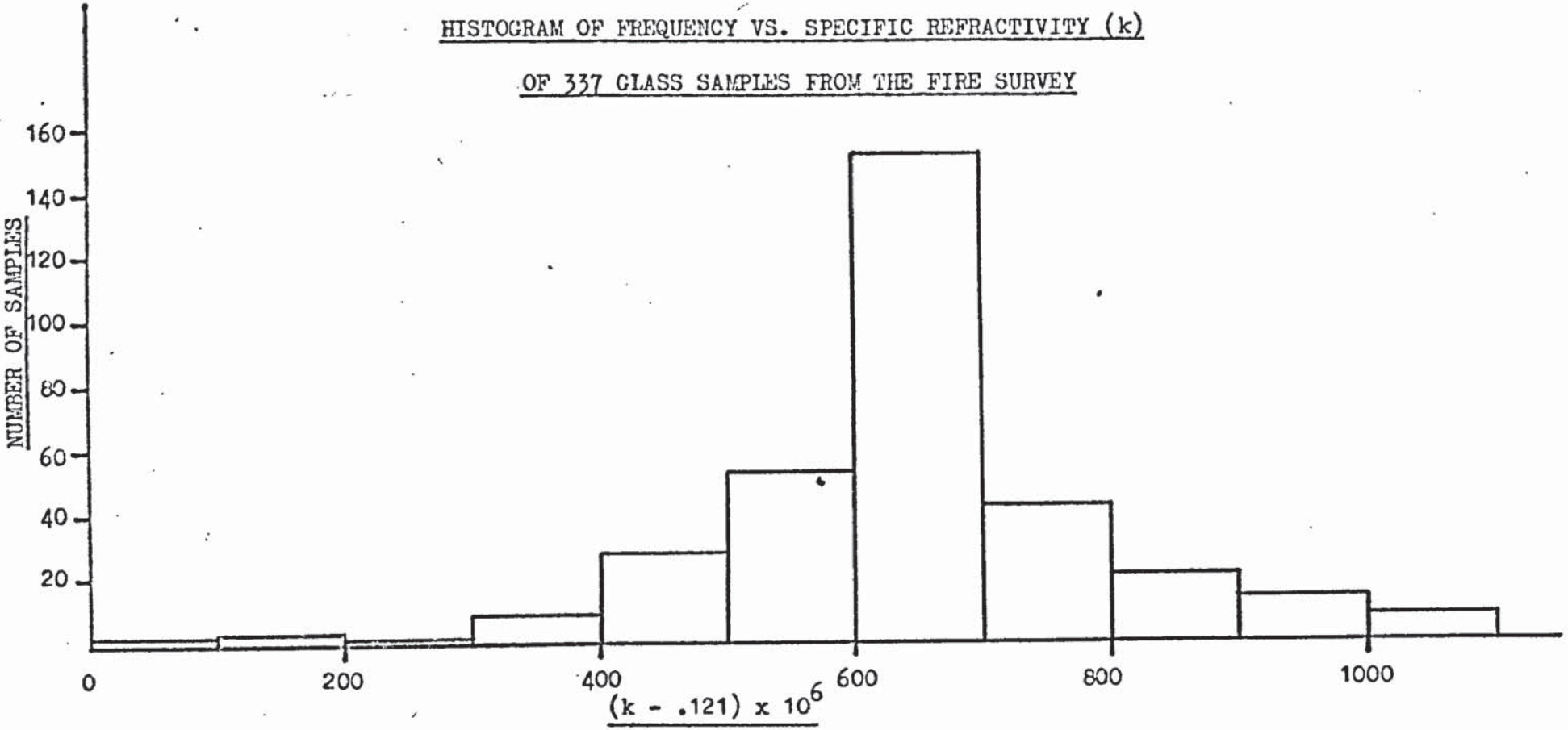


FIG. 31

HISTOGRAM OF FREQUENCY VS. SPECIFIC REFRACTIVITY (k) FOR 222 SAMPLES

FROM THE FIRE SURVEY WITH A REFRACTIVE INDEX IN THE RANGE 1.5140-1.5190

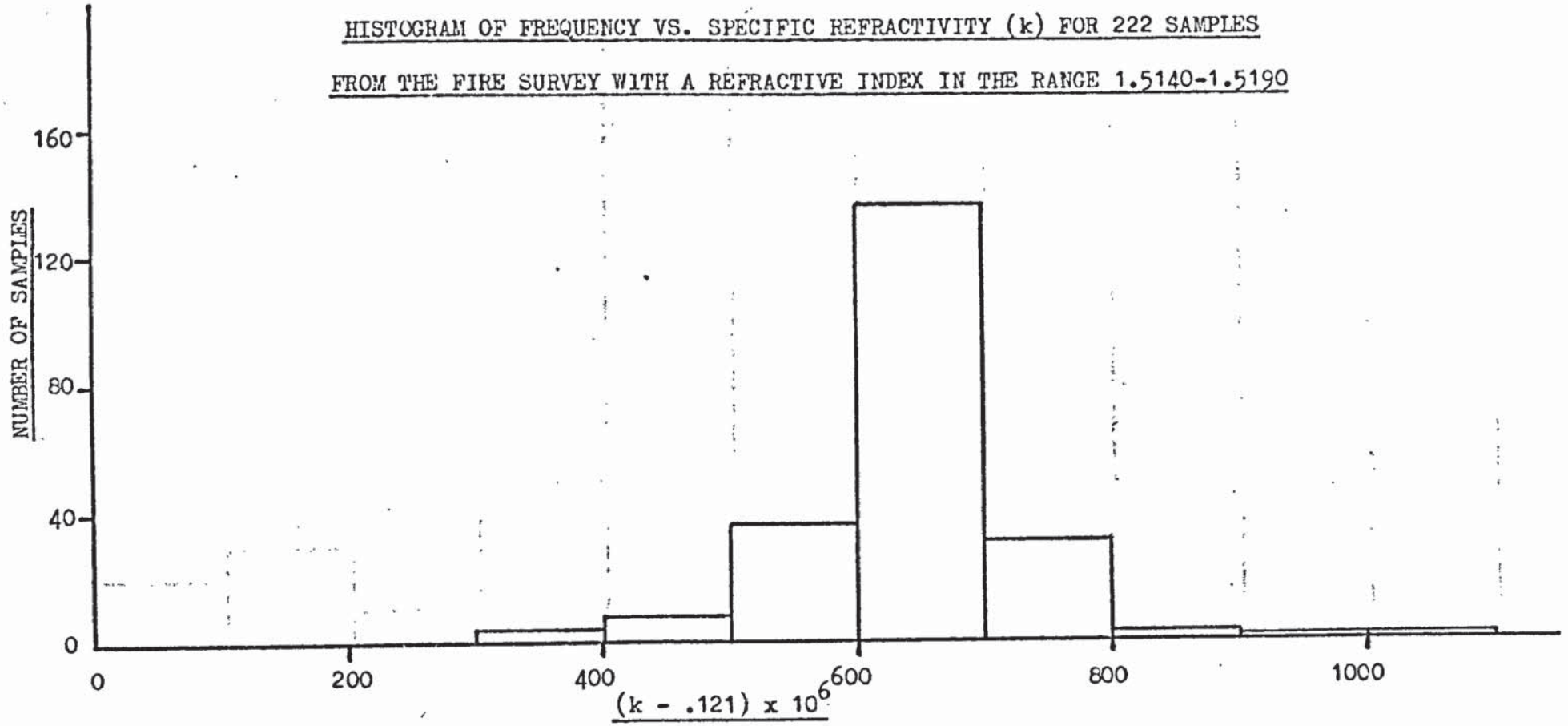


FIG. 32

HISTOGRAM OF FREQUENCY VS. SPECIFIC REFRACTIVITY (k) FOR 115 SAMPLES FROM THE FIRE SURVEY WITH A REFRACTIVE INDEX OUTSIDE THE RANGE 1.5140-1.5190

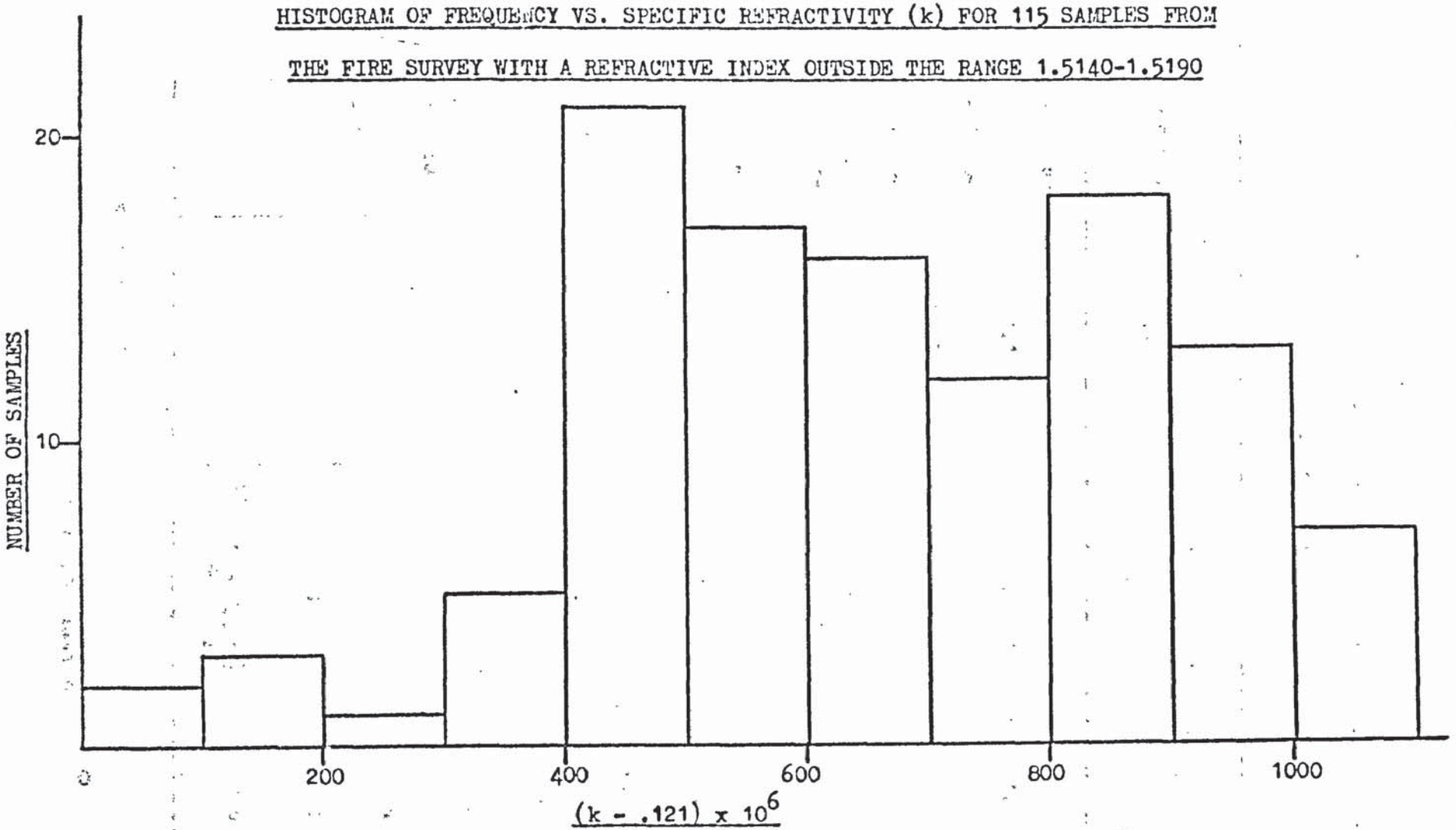


FIG. 33

TABLE 20

Comparison of the distribution of the specific refractivity with a normal distribution. Glasses with a refractive index in the range 1.514-1.519

Intervals	Number expected if distribution is normal (E)	Observed number of samples (O)	$\frac{(O - E)^2}{E}$
$\bar{x} - 2.0\sigma$			
	7.1	2	3.7
$\bar{x} - 1.6\sigma$			
	13.5	11	.5
$\bar{x} - 1.2\sigma$			
	22	14	2.9
$\bar{x} - 0.8\sigma$			
	30	16	6.5
$\bar{x} - 0.4\sigma$			
	35	40	.7
$\bar{x}$			
	35	56	12.6
$\bar{x} + 0.4\sigma$			
	30	51	14.7
$\bar{x} + 0.8\sigma$			
	22	16	1.6
$\bar{x} + 1.2\sigma$			
	13.5	11	.5
$\bar{x} + 1.6\sigma$			
	7.1	0	7.1
$\bar{x} + 2.0\sigma$			
		$\chi^2 = \sum \frac{(O - E)^2}{E}$	= 50.8

$\bar{x}$ = population mean

σ = standard deviation of population

TABLE 21

Comparison of the distribution of specific refractivity with a normal distribution. Glasses with a refractive index outside the range 1.514-1-519

Intervals	Number expected if distribution is normal (E)	Observed number of samples (O)	$\frac{(O - E)^2}{E}$
$\bar{x} - 2.4\sigma$			
	1.7	1	
$\bar{x} - 2.0\sigma$	5.4	4	.4
	3.7	3	
$\bar{x} - 1.6\sigma$			
	7	1	5.1
$\bar{x} - 1.2\sigma$			
	11	18	4.4
$\bar{x} - 0.8\sigma$			
	15	19	1.1
$\bar{x} - 0.4\sigma$			
	18	15	.5
$\bar{x}$			
	18	13	1.4
$\bar{x} + 0.4\sigma$			
	15	17	.3
$\bar{x} + 0.8\sigma$			
	11	13	.4
$\bar{x} + 1.2\sigma$			
	7	11	2.3
$\bar{x} + 1.6\sigma$			
	3.7	4	
$\bar{x} + 2.0\sigma$	5.4	4	.4
	1.7	0	
$\bar{x} + 2.4\sigma$			
		$\chi^2 = \frac{(O - E)^2}{E} = 16.3$	

$\bar{x}$ = population mean

σ = standard deviation of population

many samples in the centre of the distribution. However, because the deviation from normality in the wings of the distribution is small, little error will be incurred if this distribution is also assumed to be normal for the purpose of the statistical interpretation of results described in Section 8. The reasons why this assumption can be made will be dealt with in the same section.

The correlation coefficient between the specific refractivity and refractive index was calculated to be -0.018. The significance of this value of correlation coefficient was assessed using Student's 't', the value of which was 0.33 for 336 degrees of freedom. From tables[87] the value of t at the 25% level is 1.15. With no correlation present 't' would be as large as 1.15 in 25% of all trials undertaken. Therefore, there is no evidence to suggest that there is a significant correlation between specific refractivity and refractive index.

8. THE STATISTICAL TREATMENT OF REFRACTIVE INDEX AND DENSITY

Irrespective of the techniques of measurement used in the examination of glass fragments in forensic science, two important decisions must ultimately be made. First, and most important, it must be decided whether the two glass fragments are similar (the similarity problem) and secondly, it is helpful if some estimate can be made of the 'rarity' of the glass under examination (the identification problem). In order to examine the identification problem, it is necessary to know the parent population from which the glass has been drawn. The choice of a parent population has already been discussed, but for the purpose of this section, the Fire Survey will be used as this is the largest single survey that is available.

Parker[60,61] has already described a statistical technique to assist in solving the identification problem in forensic science, but this relies on the fact that parameters being measured must be normally distributed or be capable of transposition to a normal distribution (e.g. log normal). It may be seen from Section 6 that this is clearly not the case with the refractive index and density of glass and, therefore, it was necessary to devise a new procedure.

In the preceding section it was shown that there was a high degree of correlation between refractive index and density and, therefore, in many cases it is worth measuring only one of these parameters. However, there are occasions when there are glasses whose specific refractivity (k) is considerably removed from the mean k values for the population and in these cases, additional information may be obtained by taking both density and refractive index into consideration.

To illustrate the following statistical technique, it is assumed that a single sample has been found on the person suspected of the offence and that 10 samples of control glass has been collected from around the area of breakage in the broken window.

8.1 SIMILARITY

8.1.1. Refractive Index

The refractive indices of glasses may be compared using the Becke line technique described in Section 4.1.3. A sample from each of the controls and the sample glasses are all mounted together in a multi-cavity slide. The mean and standard deviation (σ) of the refractive index is calculated for the results obtained from the control using the following equation:-

$$\sigma^2 = \frac{\sum (x - \bar{x})^2}{n - 1}$$

where $\bar{x}$ = mean value of n determinations

x = value of the i^{th} refractive index.

To obtain a good estimate of the standard deviation, a large number of determinations should be made on the control. However, practical considerations dictate that the number of determinations made cannot be too large. The minimum number of determinations suggested here is ten, which is in agreement with the number suggested by other workers[98]. Having calculated the standard deviation, it is necessary to decide how close the sample must be to the mean of the control samples in order to classify them as similar. The wider the limits are set, the smaller will be the chance of rejecting the sample as different when it is, in fact, from the same source as the control. However, if the limits are set too wide, there is the danger that glasses quite unconnected with the control will be classified as similar to the control and this will be reflected in the discrimination obtainable. To take two extreme examples; if it is only permissible to reject a glass once in 100,000 trials when it

does in fact come from the same source as the control, then it would be necessary to classify all glasses within 4.417 standard deviations[91] of the control to be similar. However, if it is acceptable to be wrong, on average, once in every ten trials, then it is only necessary to consider glasses within 1.645 standard deviations from the control. In practice, it is more sensible to use a probability in between these two extremes. If all glasses within 2.58 standard deviations of the mean of the control are classified as similar, then the chance of rejecting a glass when it is, in fact, from the same source as the control is 1 in 100.* This is equivalent to the 'significant' probability level used extensively in statistical tests and will be used throughout this section. Therefore, if the refractive index of the sample falls within $\pm$ 2.58 standard deviations of the control, then the two glasses are classified as similar. If the sample is outside this limit, then it is stated that the two glasses are different; but there is a 1 in 100 chance that this decision is incorrect.

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* This is only true when the standard deviation is accurately known from a large number of measurements. If the standard deviation has to be estimated from the ten controls, then the above statement is not strictly true. The effect is that rather more than 1 in 100 are rejected. The matter is further discussed in Appendix 1 and elsewhere[92,99].

8.1.2. Density

Density was treated in exactly the same way as refractive index. One piece of glass was broken from each of the ten controls and a density determination made on each. The density of the sample was then determined by the same method and compared with the mean density obtained from the control glass in a similar manner to the procedure used for refractive index.

When dealing with two correlated variables, Parker and Holford[92] have suggested a technique whereby both variables and the correlation between them may be considered and this technique is fully described in Appendix 2. However, in this instance, because the correlation between refractive index and density is so high, the amount of extra work involved is seldom justified because the additional information gained will be small. Therefore, a simplified modified technique is used. The density of a large sample (over 15g) of the control is determined by weighing in air and again in water. A small fragment about the same size as the sample is then broken from the large control and placed together with the sample into a test tube containing potassium mercuri-iodide solution. The sample and control fragments are then compared using the sink-float method, as described in Section 3.1.1. The total error due to this method is the sum of the variances of the experimental method itself plus the variance due to the heterogeneity in the control sample. The variation in density due to the heterogeneity of the sample is calculated from the variation found in the refractive index using the Lorentz-Lorenz equation. The actual variation in density may be calculated for each sample from the known density

and refractive index, but it is generally sufficient to assume that the density spread will be 5 times the spread of the refractive index. Hence, the total variation of the method Σ_t is given by

$$\Sigma_t^2 = \sigma_h^2 + \sigma_m^2$$

where σ_h = standard deviation of the variation in density.

σ_m = standard deviation of the sink/float method.

or

$$\Sigma_t^2 = \left[5\,\sigma_{hn}\right]^2 + \sigma_m^2$$

where σ_{hn} = standard deviation of the variation in terms of refractive index.

The two fragments are compared using the sink/float method and if they are within $2.58\Sigma_t$ of each other, they are classified as similar. Intrinsically this technique considers all glasses within $\pm$ 2.58 Σ_t from the control, as used in refractive index, because the sign will depend on which sample rises first.

8.2 IDENTIFICATION

8.2.1. Refractive Index

A detailed plot of the Fire Survey is shown in Figure 34, each interval being 0.0001. The total area under the curve is calculated using Simpson's Rule. VIZ

$$\text{Area} = \frac{h}{3}\left(y_1 + 4y_2 + y_3\right)$$

where h = interval between points

y_1 = First ordinate

y_2 = mid ordinate

y_3 = Third ordinate

The absolute area under the curve for the Fire Survey was calculated to be 0.0934.

If the control glass has a mean refractive index $\bar{n}$ and a standard deviation σ_n then the glass in the control may be represented as a normal distribution $\left(\bar{n},\ \sigma_n\right)$ as is shown in Figure 35. The probability of obtaining a glass with the same mean and standard deviation as the control is the area under the normal curve representing the control sample divided by the area under the whole of the curve representing the population of glasses under consideration (Figure 35). However, it is not possible to determine this figure[93] because no equation relating frequency to refractive index is available.

An alternative approach is to determine the area under the curve of the population considered between the limits $\bar{n} - 2.58\,\sigma_n$ and $\bar{n} + 2.58\,\sigma_n$. If σ_n is small, the integration may be carried out in one stage using Simpson's Rule and putting

PLOT OF REFRACTIVE INDEX VS. FREQUENCY FOR THE

FIRE SURVEY SAMPLES AT 0.0001 INTERVALS

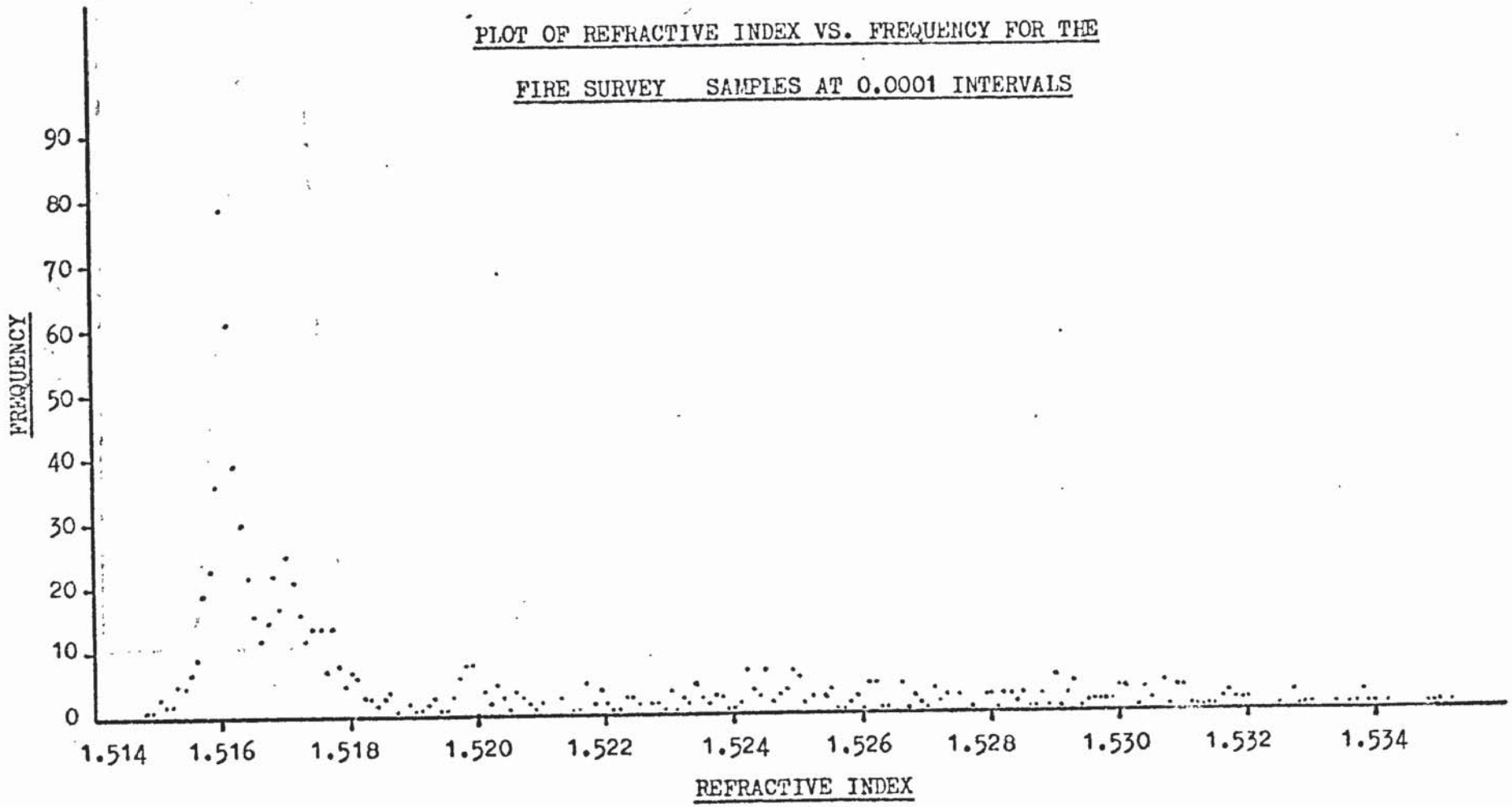


FIG. 34

SCHEMATIC DIAGRAM SHOWING HOW THE CONTROL IS THEORETICALLY SUPERIMPOSED ON THE SURVEY

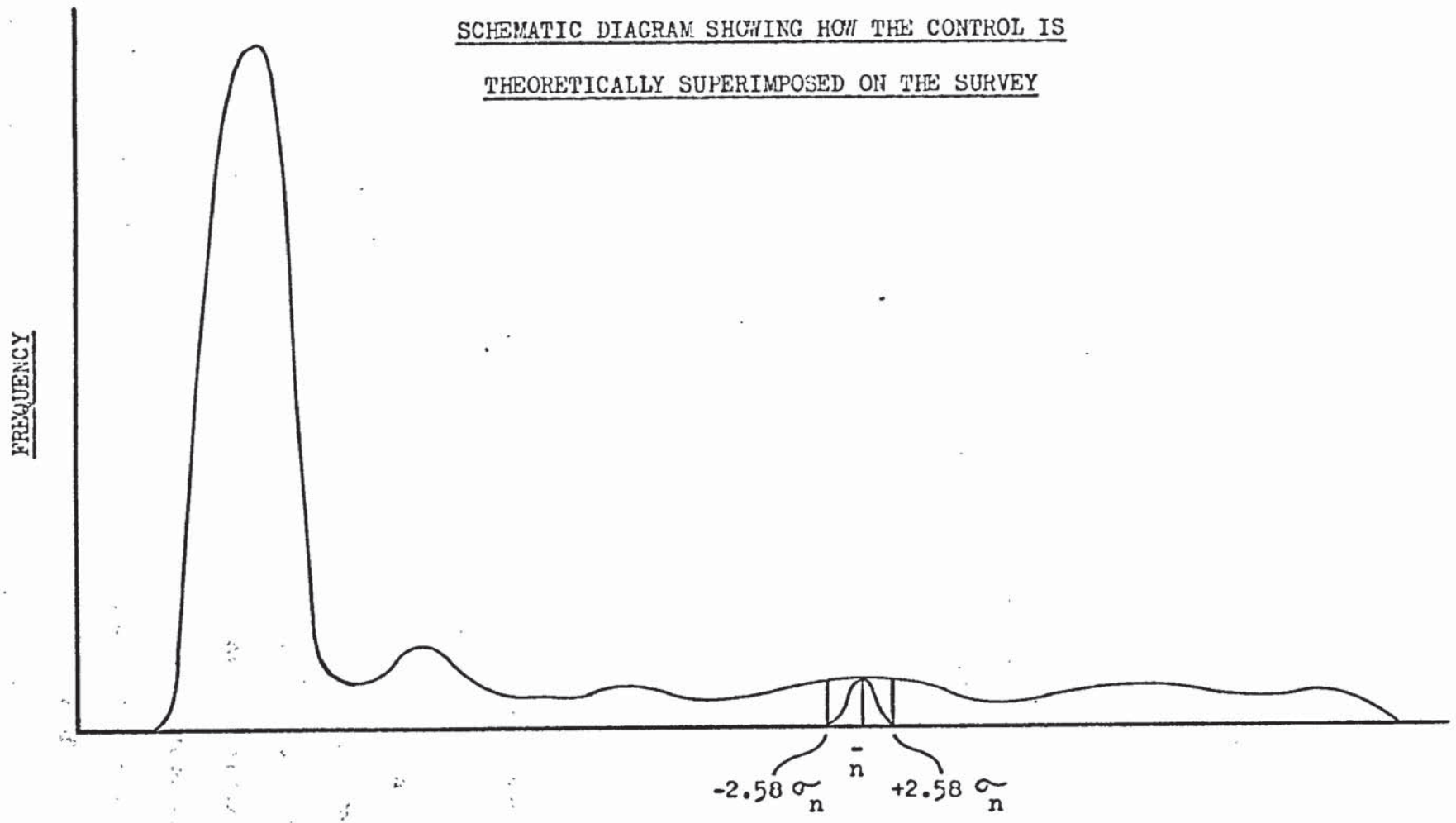


FIG. 35

$h = 2.58 \sigma_n$

y_1 = frequency at $\bar{n} - 2.58 \sigma_n$

y_2 = frequency at $\bar{n}$

y_2 = frequency at $\bar{n} + 2.58 \sigma_n$

y_1 y_2 and y_3 may be read directly from Figure 34. By dividing this area by the total area under the curve, a figure will be obtained which represents the probability that a piece of glass from the parent population under consideration will have a refractive index within the limits $\bar{n} \pm 2.58 \sigma_n$. This is a more meaningful treatment of the problem because it has already been decided to classify any glass within the limits $\bar{n} \pm 2.58 \sigma_n$ as similar to the control. The difference between the two methods is that the latter will tend to give larger probabilities (i.e. there will be a greater number of glasses of given refractive index and standard deviation in the latter case) because of the extra area that is being included.

8.2.2. Density

Because there is a high degree of correlation between refractive index and density, it is quite wrong to multiply together the probability of obtaining a glass with a particular density by the chance of obtaining a glass with a particular refractive index. However, it has been shown that the specific refractivity k (Section 7) is not correlated to refractive index (correlation coefficient - 1.8%). Therefore, if the probability of occurrence of the specific refractivity can be calculated, this can be multiplied by the value of the probability of occurrence obtained from refractive index measurements. In this way the density of the sample may be taken into account.

In Section 7 it was shown that the Fire Survey could be divided into two groups based on refractive index. The frequency distribution of k in each of these groups approximates a normal distribution and because the object of considering specific refractivity is to consider glasses that have grossly different values of k, little error will be introduced in assuming them to be normal.

The probability of occurrence of a glass with a given value of k may then be calculated in a similar manner to the calculation based on refractive index. The specific refractivity k is calculated from the Lorentz-Lorenz equation, but the standard deviation of k, σ_k cannot be measured directly and must be calculated from the known standard deviations of density and refractive index using the law of errors(94). The value of refractive index (n) is the mean of the results obtained on the control and the standard deviation σ_n is the standard deviation of the same set of measurements. The density (d) is obtained by Archimedes method and the standard deviation used this time is the standard deviation of Archimedes method ($0.0003g\ cm^{-3}$) because in this case, the glass is being compared with the survey.

From the theory of errors(94) it may be shown that if

$$u = x + y + z \quad \text{----------} \quad (1)$$

$$\text{then } \sigma_u^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 \quad \text{---------} \quad (2)$$

where σ = standard deviation of the parameter shown in the subscript.

Also, if

$$u = xy \quad \text{----------} \quad (3)$$

$$\text{then } \sigma_u^2 = y^2 \sigma_x^2 + x^2 \sigma_y^2 \quad \text{----------} \quad (4)$$

and if $u = \frac{x}{y}$ - - - - - - - - - - - - - - - (5)

then $$\sigma_u^2 = \frac{\sigma_x^2}{y^2} + \frac{x^2}{y^4}\,\sigma_y^2 \quad \text{- - - - - - - - - (6)}$$

Considering the Lorentz-Lorenz equation where

$$k = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \quad \text{- - - - - - - - - (7)}$$

Putting $n^2 = N$ - - - - - - - - - - - - - - - - (8)

$$k = \frac{N - 1}{N + 2} \cdot \frac{1}{d} \quad \text{- - - - - - - - - - (9)}$$

and putting $N - 1 = A$ - - - - - - - - - - (10)

and $N + 2 = B$ - - - - - - - - - - (11)

k can now be expressed in the simplified form

$$k = \frac{A}{Bd} \quad \text{- - - - - - - - - - - - - - - - (12)}$$

The standard deviation of all terms on the right hand side of the equation may now be calculated and used to determine the standard deviation of k.

From 1, 2 and 10 it may be seen that

$$\sigma_A^2 = \sigma_N^2 \quad \text{- - - - - - - - - - - - - - (13)}$$

because 1 is a constant with zero standard deviation. Also from 3, 4 and 8

$$\sigma_N^2 = 2n^2\,\sigma_n^2 = \sigma_A^2 \quad \text{- - - - - - - - (14)}$$

and similarly

$$\sigma_B^2 = 2n^2\,\sigma_n^2 \quad \text{- - - - - - - - - - - (15)}$$

From 3, 4 and 12

$$\sigma_{Bd}^2 = d^2\,(2n^2\,\sigma_n^2) + B^2\,\sigma_d^2 \quad \text{- - - - (16)}$$

$$\sigma_k^2 = \frac{2n^2\ \sigma_n^2}{\left[d(n^2+2)\right]^2} +$$

$$\frac{(n^2-1)^2}{\left[d(n^2+2)\right]^4}\left[2d^2\ n^2\ \sigma_n^2 + \sigma_d^2\ (n^2+2)^2\right] - - - -(17)$$

Hence k and σ_k may readily be calculated.

Because the distributions of k for both groups of glasses are assumed to be normal, the area under the curve may either be calculated on a computer or looked up in normal probability tables. This has the advantage that points do not have to be read off a graph. Consider Figure 36. This shows a graph of a normal probability distribution which applies to both groups of glasses. μ is the population mean and σ_p is the standard deviation of the population. $\bar{x}$ represents the specific refractivity of the sample and σ_s is the standard deviation calculated using equation 17. Again 2.58 standard deviations are chosen, each side of the sample mean $\bar{x}$. The probability of obtaining a glass whose specific refractivity falls within the range $\bar{x}$ - 2.58 σ_s and $\bar{x}$ + 2.58 σ_s is given by dividing the area between these two points by the total area under the curve. To do this it is necessary to define the two limits $\bar{x}$ - 2.58 σ_s and $\bar{x}$ + 2.58 σ_s in terms of the number of population standard deviations they are away from the population mean μ. Therefore, the upper limit is given by

$$\frac{\bar{x} + 2.58\,\sigma_s - \mu}{\sigma_p}$$

and the lower limit by

$$\frac{\bar{x} - 2.58\,\sigma_s - u}{\sigma_p}$$

THE NORMAL PROBABILITY CURVE REPRESENTING THE DISTRIBUTION OF SPECIFIC REFRACTIVITY FOR BOTH GROUPS OF GLASSES

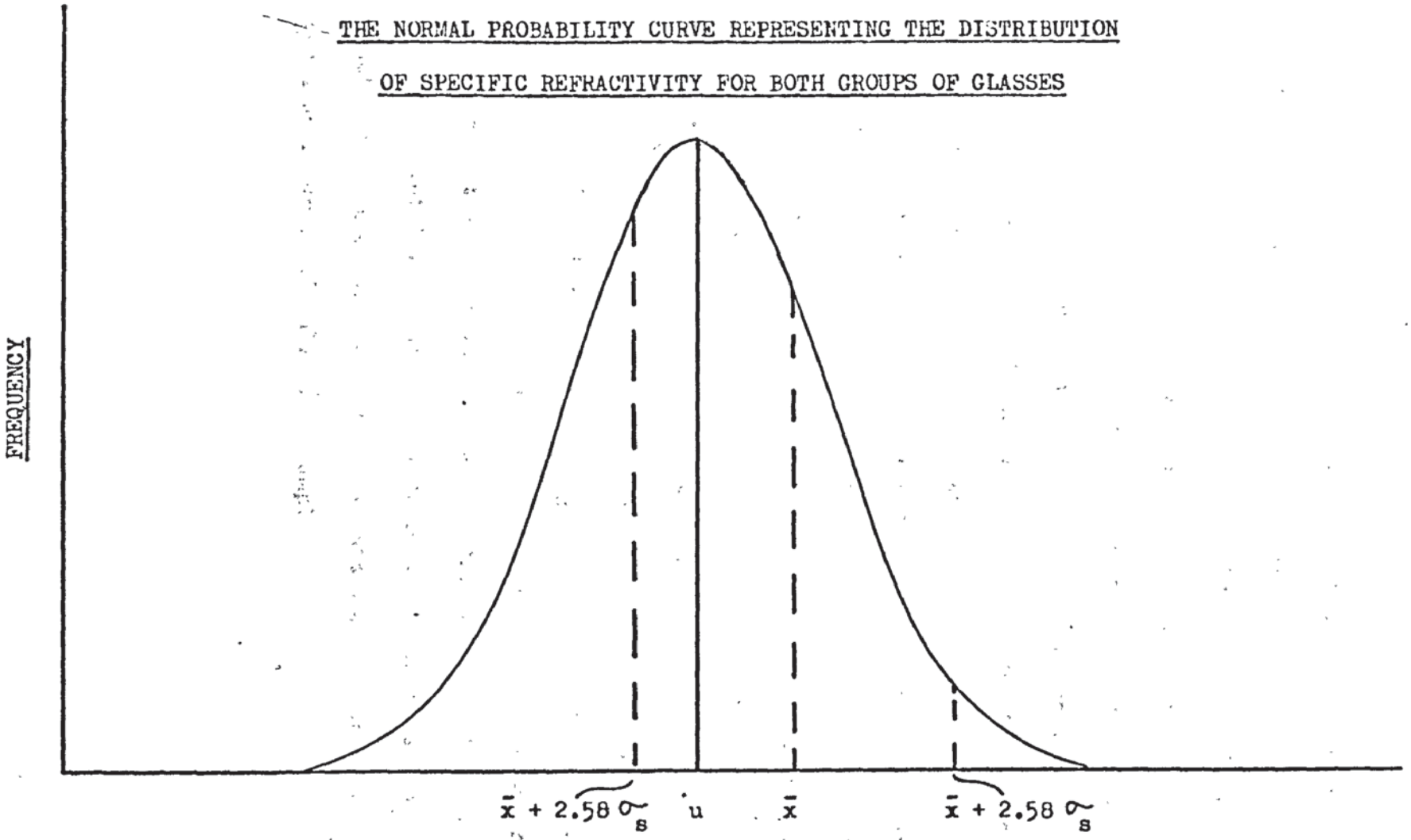


FIG. 36

The area between these two limits may then be computed or read from normal probability tables[87].

This additional information must be used carefully. Theoretically the probability of obtaining a glass with a given refractive index (p_n) can be multiplied by the probability of obtaining a glass with a given specific refractivity (p_k) to give the total probability p_t. However, the fact that only 1,000 glasses have been sampled must be taken into account, especially when the sample lies in the tails of the distribution and only a few samples were found in each interval during the survey. Therefore, especially at the extremes of the distribution there is an uncertainty attached to the probability of occurrence calculated from both refractive index and specific refractivity. Because of this, there is an uncertainty attached to the total probability p_t and it would imply too much precision in the value of p_t if a value of $p_k = 0.5$ was taken into consideration. It would be more desirable to ignore p_k unless the specific refractivity of the sample is 2 standard deviations or more away from the mean of the population. In effect this means that p_k is not considered until it is around 0.1 or less. In any case, p_t should not be quoted less than 0.001 when the statistics are based on a survey of only 1,000 samples.

PART 2.

MASS SPECTROMETRY.

9. INTRODUCTION

J. J. Thomson first demonstrated the principle of mass spectrometry in 1912 and in 1919 Aston built the first mass spectrograph using a similar geometry to that used in present day apparatus.

It was not until the late 1950's when commercial spark source instruments became readily available that spark source mass spectrometry became established as an analytical technique.

An early paper by Hanney and Ahearn[101] discussed some of the general considerations of spark source mass spectrometry. For quantitative results they suggested plotting the log of the absorbance of the line vs. log of the exposure in a similar manner to the Wagner plot described by Schuy and Franzen[205]. Even as early as this (1954), they pointed out the advantages of using electrical detection for quantitative work.

Brown, Craig and Elliot[102] stated that for over half the elements the detection limits were below 0.003ppm and detection limits as high as 0.1ppm were rare, but there were certain factors which could raise this limit. These figures are in broad agreement with those reported by Wolstenholme[158,161]. Saunders[157] points out that the sensitivity of the spark source technique has been reported to be between 1 part in 10^8 and 3 parts in 10^{10}. Sensitivities of various elements were reported to vary by not more than a factor of 3 which agrees with the findings of other workers[104, 113, 158]. Using microphotometric comparison a relative standard deviation of 20% was reported. Over a limited region of the plate reproducibilities of the order of $\pm$5% were obtained compared with a factor of 2

using visual examination. Halliday, Swift and Wolstenholme[104] have reported the standard deviation of the ratio of $^{107}Ag^+$ ions, to $^{109}Ag^+$ ions, to be 3.7% for 15 identical exposures on the same Ilford Q2 plate. This value rose to 5.8% for the same exposure on 8 separate plates. However, the variations would normally be greater as sparking conditions (pulse length and repetition rate) are altered. A formula was given to calculate the volume of sample consumed for a required analysis and it was shown that between 10^7 and 10^8 atoms are consumed for each ion delivered to the photoplate. Craig and Wolstenholme[161] have shown that 6,000 ions are necessary to produce a "just detectable image" on an Ilford Q2 plate while elsewhere Wolstenholme[158] reports the figure to be between 6,000 and 20,000 ions. Honig[105] has reported that about 1×10^5 ions/mm^2 are required to produce a just detectable image on Ilford Q2 and Kodak SWR plates, but that at 50% transmission the latter is about 3X more sensitive due to the steeper slope of the response curve. Honig has listed several ways of producing ions from solids by methods other than the R.F. spark discharge and has pointed out the advantages of using focused radiation to vaporize the sample. However, the sensitivity is not as good as reported elsewhere[104] for the R. F. spark discharge. He also showed that when using an Associated Electrical Industries (A.E.I.) MS7 mass spectrometer the energy distribution of impurity ions in a sample of iron were all similar and this explains why analyses made on the MS7 are not seriously affected by changes in the ion accelerating potential. This is at variance with the findings of Franzen and Hintenberger[106].

The vibrating arc works well for solid conducting electrodes, but not at all for insulators or fragile materials. Honig also showed that the response of Ilford Q2 plates is related to mass by the equation $R = kM^{-0.6}$ which is somewhat different to the relationship reported by Owens[212]. Line lengths and widths must be taken into account and it was found that line length increased from the low end to the high mass end of the photoplates. A relative standard deviation of 30% or better was obtained, but absolute accuracy depended on the availability of suitable standards.

Many different materials have been analysed by mass spectrometry. Bulk and surface impurities in insulators have been examined by Ahearn[107] and biological materials by Evans and Morrison[108]. Geological materials have been examined by several workers[109,112,113,117,138] on a variety of instruments. By taking stringent precautions to prevent contamination, Leipziger and Giudoboni[110] determined nitrogen, oxygen and hydrogen in various metal samples. Results were converted to weight ppm using the formula

$$\text{wt. ppm} = \text{at. ppm} \left(\frac{\text{atomic wt. of impurity}}{\text{average atomic wt. of matrix}} \right)$$

Mercury has been determined in apples[115] and Scala, Sweeney and Hickam[116] have analysed stearate layers containing metal ions. Mass spectrometry has also been used to analyse dried blood plasma[137], dental tissues[207], gallium[142], iron[149], liquids[153], polyurethane resins[176], rare earths[127,155] and miscellaneous materials[128].

Techniques for the reduction of surface contamination of the sample have been described[130] and other workers[131] have analysed crystals of insulating materials using a tantalum auxiliary electrode when the tantalum content of the ion beam was reported to be less than 1% (c.f. ref[124]). Isotope dilution, isotopic abundance and the dating of minerals have been studied[132] and Jensen, Goshgarian and Dane[134] have examined rocket fuel combustion products using a CEC 21-110 mass spectrometer. A press for use with powdered samples as small as 0.1mg has been reported[135] and good results were obtained on samples of ashed hair and fibres.

Small chunks of glass have been analysed by Desjardins and Williams[119], by sparking against a gold counter electrode, and by Swift[120], who supported the glass slivers in indium electrodes and by Jackson[121], all using MS7 instruments.

Sensitivity factors are generally quoted by reference to iron[104,113,157,158], but copper[108], nickel[164], and niobium[168] have also been used.

Internal standards should possess a number of properties and these have been listed and discussed[112]. Among internal standards used rhenium[109,112], silicon[113], silver[115], indium[117] and iron[153] may be mentioned.

The loss in sensitivity when using a vacuum vibrator source (D.C. vibrator arc) are reported to be small[111]. Other workers[122] also claim advantages for D.C. arc sources. Some of the advantages that have been quoted[111] include simpler electronics, smaller ion energy spread and sharper lines (and hence higher resolution and greater sensitivity). In addition, a

smaller quantity of gas is produced during sparking and the use of electrical detection is easier because of the absence of R.F. interferences.

Cryosorption pumping in the mass spectrometer has been tried by several workers[114,115,119,130]. Harrington, Skogerboe and Morrison[114] using a GRAF-2 mass spectrometer report markedly reduced interferences in the mass spectrum eliminating many of the doublets and triplets which occurred at some mass numbers. In addition, the relative standard deviation was reduced from 51.8% to 19.6%. Tong et al[115] and Desjardins and Williams[119] have used cryosorption pumping in a MS7 and Socha and Willardson[130] have used it in both source and collector regions in addition to diffusion pumps.

A recent paper by Morrison and Kashuba[117] described the analysis of basaltic rock using a GRAF-2 mass spectrometer in preparation for the analysis of lunar materials. The results showed a relative standard deviation of from 5-25% and an average accuracy of 14% for major and trace elements. Indium was used as an internal standard and graphite or silver as the supporting matrix. The material was pressed into a flat disc 11mm in diameter and 1-2mm thick. The disc was then quartered and mounted. It was reported that this type of electrode enhanced the formation of M^+ ions and improved precision. A Hewlett-Packard HP9100 calculator was used for the calculation which was similar to that described elsewhere[108]. Good agreement between results obtained by neutron activation and mass spectrometry were reported especially in the range 1-1000ppm. For ultra-trace elements below 1ppm the agreement was not so good because at these levels

all techniques were claimed to give poor precision. Evans and Morrison[118] have claimed that the use of time resolution improved the analytical uses and increased precision.

Jackson, Whitehead and Vossen[146] have described the use of ion beam chopping to increase the precision of estimation of major constituents. Ion beam chopping allows very short exposures to be taken without the effects of heterogeneity in the sample causing trouble. These workers demonstrated that by increasing the ratio of the time interval between pulses to the duration of each pulse the precision of the results increased to about 5% for phosphorous and calcium in titanium dioxide in the exposure range 10^{-12}C to 10^{-11}C. Again using an ion beam chopper Jackson[121] claimed a precision of 5-10% relative standard deviation for powdered samples containing homogeneously distributed impurities. Without this attachment the values were 10-20%. Vossen[147] has used this technique for the analysis of steel and aluminium and increased precision from 33.4% to between 10-20%. Brown, Swift and Vossen[133] also report good results using ion beam chopping.

Franzen and Schuy[122] have reviewed precision in spark source mass spectrometry. They pointed out the main factors affecting precision and recommended the use of a low voltage discharge source. Relative standard deviations of about 5% were reported for elements which were homogeneously distributed through the sample.

Useful special techniques for the preparation of powdered samples have been described[123,124]. In addition, it has been found[124] that sparking against a gold electrode pro-

duced less than 5% gold in the ion beam. Owens[125] has pointed out the advantages of using metal powders as the supporting matrix, but warns that more multiple ionization occurs with a silver matrix.

High background levels interfere with the detection of some elements near the limit of detection. Mai[126] has investigated this problem and has found that the suppressor plate fitted to the MS7 is only effective when the monitor current is below $3x10^{-10}$amp. However, it has been pointed out[161] that ion currents of about 10^{-9}amp are feasible with the spark source and even higher currents are attainable with the D.C. arc. Craig and Wolstenholme[161] conclude that in practice ion currents greater than 10^{-8}amp are limited by space charge effects and surface charging of the photoplate. Mai found that by cutting out those areas of the photoplate receiving the most intense lines, it was possible to entirely suppress the 'halo' caused by these lines.

Chamberlain[129] and McCrea[139] have considered the errors involved in the photometry of photoplates and suggest limits within which the method precision (coefficient of variation) can be kept to 5% or less. McCrea has also given an equation which represents the response of many photoplates and is, in fact, a generalized form of the Hull equation[200].

Elemental associations in the spark source have been studied[136] and it was shown that the electrode held at the higher positive potential was preferentially ionized. Wolstenholme[158] has stated that for an MS7 the intensity of multiply charged ions decreases by a factor of 3 to 30 for each degree of ionization. Polyatomic ion formation is generally very low, but

carbon, beryllium, aluminium and silicon form larger numbers of polyatomic ions. Complex ions (e.g. $FeOH^+$) are sometimes formed, but always at low intensity. The overall intensity of complex and polyatomic ion formation could be reduced by reducing the spark voltage and pulse length. However, Cook[154] has investigated the formation of polyatomic ions and reports that for molecular ions of the type C_n^+ and C_n^{2+} the intensity is quite independent of the excitation conditions and the wider the electrode gap the more polyatomic ions were found to be produced. Craig and Wolstenholme[161] has shown that the D.C. arc produced more multiply charged ions than the R.F. spark. Goshgarian and Jensen[166] have studied the relationship between the relative concentration of polyatomic species formed in the spark ionization, with bond characteristics. Woolston and Honig[186] have examined the theory behind the energy distribution of ions formed in the R.F. spark. They have also studied the energy distributions of ions formed in different materials and have concluded that various matrix materials exhibit different ion energy distributions under equivalent conditions. Nickolls et al[112] have also reported matrix effects to be important in that they effect sensitivity factors considerably. In addition, the distributions were affected by source parameters such as spark voltage and gap width. The accelerating voltage must be well regulated. In a later paper[187] it was shown that for a given element the energy distributions were similar whether the element was there as a trace or as the matrix. In addition, it was found that the energy distribution increased with increasing R.F. spark voltage and multiply charged ions exhibited very similar distributions to

singly charged ions of the same substance.

An analogue computer, similar to that used by other workers[130] has been used by Paulsen and Branch[140] who point out the importance of taking line widths into account. Improved precision was reported when area measurements were used.

Williamson and Harrison[141] have compared the use of neutron activation analysis and spark source mass spectrometry for the analysis of hair for forensic applications. They found that silver powder formed more stable electrodes which sparked more profusely than graphite (cf. Conzemius et al[155]). Agreement between the two methods was generally good, but mass spectrometry required $\backsim$ 0.5g of hair prior to ashing for incorporating into electrodes.

Campbell and Adams[143] have evaluated the problems in the analysis of trace elements in glasses and Brown and Wolstenholme[144,145] have set out some general considerations concerning the analysis of insulating powders and have shown the resolution required to separate certain elements from carbon molecular ions occurring at the same nominal mass number.

Saunders[157] has suggested ways of overcoming heterogeneity effects and has considered some of the general problems relating to detection limits in spark source mass spectrometry in contrast to Addink[156] who has studied detection limits for a variety of techniques. Elliot and Swift[189] have also described a novel technique for the estimation of detection limits and Keene[159] has briefly reviewed some of the most important points in mass spectrometry.

Ahearn[164] has reviewed some of the methods available for handling various types of sample. Hickam and Sweeney[162] have described some work they have carried out using a spark source mass spectrometer for the microanalysis of solids (mass spec. microprobe) and insulating materials[163] and tobacco ash[167] have also been studied. Jackson and Whitehead[168] have experimented with graphite, silver and gold as the matrix material and Dietze[148] has reported good results using aluminium. Gold was least satisfactory from the mechanical viewpoint. It also gave an intermittent spark and took about 4 times as long as graphite or silver to collect the same charge. The use of peak areas was reported not to improve the results which is contrary to the finding of Skogerboe et al[169] who has reported good results using transmittance areas.

Berry[150] and Hintenberger[151] have discussed a "figure of merit" that may be applied to mass spectrometers incorporating both its resolution and transmittance. Hull[152] has expanded the 'figure of merit' idea of Berry and Hintenberger and subjected it to extensive mathematical treatment.

McCrea has examined the characteristics of Ilford and Kodak photoplates[170] and recommends Ilford Q2 photoplates developed in ID 19[171]. However, he reports that in certain conditions the developer suggested by Kennicott[172] has advantages. Grais[177] has also studied Ilford photoplates and gelatin free ion sensitive plates have been prepared[183]. McCrea[173,174] has described a photographic indexing technique for quality control purposes. The sensitivity of mass spectrographs and ion sensitive photoplates has been considered[175,176]. Perkins[179]

has described a precision plate reader for the accurate determination of mass numbers and Owens[180] has reported an improvement in precision using a simple mechanical developer for photoplates. The response of ion sensitive photoplates as a function of energy has been studied[181,182] and Owens[212] has found that for Q2 plates the log of the opacity of the spectral line is approximately proportional to the log of the ion energy. The relative sensitivity due to mass for Q2 plates was found to be similar to the relationship given by Burlefinger and Ewald[184]. Multiply charged ions with a charge q have q times the energy of the accelerating voltage and, therefore, were apparently more sensitive, but sensitivity varied from plate to plate.

Skogerboe, Kashuba and Morrison[185] point out that precision is limited by densitometer error and that emulsion nonuniformities are of secondary importance which agrees with the findings of Franzen and Schuy[122].

As early as 1951 Gorman, Jones and Hipple[165] described the use of electrical detection using a modified double focusing mass spectrometer. These workers varied the magnet current so that ions of various masses were swept past a stationary collector. Only elements present in relatively large amounts were considered and the results were expressed as a ratio to the concentration of iron. The precision was quoted as the range of measurements in percentage of the mean value and ranged from 2% to 10% for nickel and chromium. Argyle and Bingham[190] have described some basic experiments with electrical detection in a spark source mass spectrometer and have reported increase sensitivity and precision. Conzemius and Svec[191] have also studied

the use of electrical detection and report precisions of between 1% and 10%. In addition, good results were obtained for small volumes of heterogeneous materials. Both peak switching and peak scanning modes of operation were available on the Graf 2.2 mass spectrometer used. Bingham and Powers[192] have described an electrical detection system for an A.E.I. MS702 mass spectrometer. In the scan mode the system could detect elements at concentrations between 0.2ppm and 200ppm, a complete scan taking as little as 3 minutes with a mean precision of 35% (for a copper standard). In the peak switching mode the precision for copper standards ranged from 2.7% to 7.6%. An analysis time of 7½ minutes for 10 elements was said to be typical. In addition, it was shown that with only a 0.1nC integrated monitor charge it was possible to detect an isotope of lead which was present in a rock sample at a concentration of 7ppb. Evans, Guidoboni and Leipziger[193] have also used an A.E.I. MS7 mass spectrometer with electrical detection. A microscope was used to assist in setting up the electrodes and a precision of 3% relative standard deviation was reported.

The reported precision obtained by various workers using spark source mass spectrometry as an analytical technique varies widely. Some workers[112,122,138,146] have reported an excellent precision of around 5% while others[132] have obtained precisions as low as 44%. However, a more usual precision appears to be in the region of 20%[105,144,157,167,168].

Many different methods of photoplate interpretation have been used. The Seidel function has been used by several workers[108,118] and others have used the Churchill 2-line method[131,155]. The Hull equation has also been used[109,134,

153) and a generalized form of the Hull equation has been described by McCrea[139,170]. The use of peak areas has also been examined[114,124,168,169]. Anderson and Lincoln[178] have used a mathematical approach to emulsion calibration in optical spectroscopy and have pointed out the usefulness of small desk computers.

Evans and Morrison[108] have used a computer programme to perform a least squares fit of the Seidel function vs. the logarithm of the exposure for the internal standard. The emulsion response curve was then used to obtain the background corrected response curve for the calibration isotope. The internal standard calibration curve was iteratively corrected for background as long as the slope and intercept changed by more than 1%. Background corrections were then made for the impurity lines and the exposure required to produce lines of the same intensity as the standard determined. The method was similar to the approach used elsewhere[117]. The relative standard deviation obtained generally ranged from 17 to 31% and it was found that the addition of yttrium or lanthanum as internal standards produced intensity and reproducibility problems.

Desjardins and Moore[194,195] have described a method for the interpretation of spark source data. They constructed their calibration curve by plotting optical density vs. log(exposure x abundance) of the matrix element. This curve was then shifted horizontally until an optical density value of 0.2 corresponded to a value of 10 on a new intensity scale which was directly proportional to the exposure scale. This calibration curve was then used to convert optical density to ion intensity.

Any optical densities over 0.7 were ignored. For an unknown the log intensity values (read from the calibration curve) were plotted against log exposure to give a slope of 45°. A ruler graduated in the inverse of the exposure scale was placed on the graph and the exposure at a standard optical density read off. The ratio between this value and a similar value obtained for the matrix was then determined. The method was similar to both the Churchill and Wagner methods of plate calibration and a computer programme in FORTRAN IV was also described.

An interesting paper by Owens[196] reviewed the development of spark source mass spectrometry to date and discussed some of the methods of photoplate interpretation. Owens[197] has also examined several aspects of photoplate detection and Owens and Giardino[198] have studied quantitative analysis using mass spectrometry. Calibration was based on the Churchill[199] method and procedures were described to take both line width and ion mass into account. However, Franzen and Schuy[203] have pointed out the dangers of using the Churchill 2-line method with ion-produced images and in any case, this procedure is only applicable to elements whose abundance ratio falls within the requisite range.

An early paper by Craig, Errock and Waldron[160] described a prototype MS7 spark source mass spectrometer. For accurate work peak height was plotted against log exposure and the exposure required to give a certain line density was determined for both impurity and standard. This procedure has also been used elsewhere[112].

Schuy and Franzen[205] have pointed out the applicability of Wagner's[208] approach to the interpretation of mass spectrometric photoplates. The log(absorbance) was plotted against log(exposure) and Wagner has shown that this should yield a straight line of slope = 1 for low levels of blackening on the photoplate. Because Wagner's method only gave a straight line when there was a small amount of line blackening background correction was very important. Schuy and Franzen[205] have suggested that background may be corrected for by assuming that:-

$$A_l = A_{lb} - A_b \quad \text{- - - - - - - - - - - - - - - - - -} \quad (1)$$

where A_l = absorbance due to isotope being measured

A_b = absorbance due to background

A_{lb} = absorbance due to isotope plus background

The Seidel function is well known in emission spectroscopy and has also been applied to mass spectrometry. However, even in emission spectroscopy the Seidel function did not always give completely straight lines. Kaiser[209] has suggested a way to overcome this problem when using the Seidel function and other workers[210] have used this technique in emission spectroscopy. Kaiser used a factor f in his equation which was adjusted between the limits 0 and 1 for each plate to produce the straightest line. The Kaiser equation is given by

$$K = (1 - f) \log_{10}\left(\frac{100}{T}\right) + f \log_{10}\left(\frac{100}{T} - 1\right) \quad \text{- -} \quad (2)$$

where T = percentage transmission. When the correct value of f is chosen a plot of K vs. log E should yield a straight line over most of the transmission range.

Paulsen[211] found that the Seidel function produced curved lines when used with ion produced images. He worked in terms of absorption (κ) and plotted

$$\log \left(\frac{1}{1-\kappa} - 1\right) \quad \text{vs} \log E.$$

However, he found that if he divided all the values of κ by the absorption of the line at plate saturation (κ_s) then he obtained a linear relationship for all values of absorption.

Franzen, Maurer and Schuy[204] have derived a theoretical equation to describe completely the transmission curve of ion sensitive photoplates. These workers used a computer programme[203] to evaluate T_l where:

$$T_l = T_s + \frac{1 - T_s}{\left[1 + \frac{eN}{v(1 - T_s)}\right]^v} \qquad \text{----------} \quad (3)$$

where T_l = line transmittance

T_s = saturation transmittance

e = photographic sensitivity

N = number of ions incident per unit area

V = a parameter of the size-frequency distribution of the AgBr grain impact areas. V governs the slope of the transmittance curve.

Background correction was carried out using equation 4

$$T_l = 1 - \left[\frac{(T_b - T_l + b)\,(1 - T_s)}{(T_b - T_s)}\right] \qquad \text{------} \quad (4)$$

where

T_l = line transmittance corrected for background fog.

T_b = transmittance of background fog.

T_{l+b} = transmittance of line plus background as measured with the microdensitometer.

The sensitivity loss of the photoplate due to background fog was given by

$$\varepsilon = \left[\frac{T_b - T_s}{1 - T_s}\right]^{\frac{1}{v}} \quad \text{----------} \quad (5)$$

where $\varepsilon = \frac{e_{corr}}{e_{uncorr}}$ = factor of the sensivitity loss and

e_{corr} and e_{uncorr} = photographic sensivity after and before correction.

The relationship connecting the ion density N producing a given line with the concentration C of a given element in the sample was given by

$$N = \frac{C\ s\ E\ h}{b\ l} \quad \text{----------} \quad (6)$$

where C = concentration of a particular element in the sample.

s = relative sensitivity of the ion formation and extraction process for a given element and charge, referred to the sum of all ions in the beam arriving at the monitor detector.

E = exposure of the photoplate as measured by the monitor-detector.

h = isotopic abundance.

b = effective line breadth.

l = effective line length which is equal to the length that would appear were there no limiting apertures in the beam.

The photographic sensitivity e was given by

$$e = e_{abs} \cdot e_{rel} \cdot \varepsilon \quad \text{- - - - - - - - - - - - - - - - (7)}$$

where e_{abs} = absolute sensitivity of the photographic plate for ions of mass 1 and energy 1.

e_{rel} = sensitivity of the photoplate for ions of given mass and energy relative to ions of unit mass and energy.

ε = factor of sensitivity loss of the photoplate due to background fog.

The term eN in equation 3 was defined as

$$eN = q_1 P_1 \quad \text{- (8)}$$

The first term was defined by

$$q_1 = \frac{e_{rel}\, \varepsilon\, h\, E}{b\, l} \quad \text{- - - - - - - - - - - - - - - - (9)}$$

all terms on the right hand side of the equation being known. q_1 may be considered as a "normalized exposure".

The second term P_1 was defined as

$$P_1 = C\, e_{abs}\, s \quad \text{- - - - - - - - - - - - - - - - - -(10)}$$

All the terms on the right hand side of the equation were unknown, but by arranging the experimental data such that two of the terms cancel out the remaining term could be

evaluated. In this work only the relative concentrations were considered and, therefore, e_{abs} and s were taken as unity.

Equation 3 may be written in the form

$$\frac{1 - T_s}{T_l - T_s} = \left[1 + \frac{eN}{v(1 - T_s)}\right]^v \quad \text{- - - - - - - - -} \quad (11)$$

Taking roots and rearranging gives

$$\frac{eN}{v(1 - T_s)} = \left[\frac{1 - T_s}{T_l - T_s}\right]^{\frac{1}{v}} - 1 \quad \text{- - - - - - - - -} \quad (12)$$

Substituting equation 8 into equation 12 and rearranging gives

$$P_l = \frac{v(1 - T_s)}{q_l}\left[\left(\frac{1 - T_s}{T_l - T_s}\right)^{\frac{1}{v}} - 1\right] \quad \text{- - - -} \quad (13)$$

Equation 13 is different from the equation for P_l given by Franzen and Schuy[203], but the equation given in this reference almost certainly contains a printing error.

Franzen and Schuy used a Siemans 2002 computer to plot the transmission curve and a least squares procedure was used to find the best fit. If an exact fit was not obtained v and T_s were altered in small increments until the minimum sum of squares was obtained. However, they reported that the process was time consuming even by computer and, therefore, they only determined v once per analysis.

Franzen and Schuy[122,203] have claimed that by using the above equations good precision (better than 5%) can be obtained from a series of photoplates. However, Goshgarian and Jensen[166] have reported that they obtained disappointing

results when using the equation of Franzen and Schuy. Franzen and Schuy have also reviewed[205] methods available for the quantitative evaluation of photoplates and conclude that the method that they have described elsewhere[203,204] gives better precision, especially when dealing with multiply charged ions.

An empirically derived equation describing the entire transmission curve has been given by Judson and Hull[200] and Woolston[201,202] has written a computer programme based on this equation. They proposed that the following equation held true for ion sensitive photoplates

$$\frac{T_l - T_s}{1 - T_s} = \frac{1}{1 + (KE)^R} \qquad \text{- - - - - - - - - - - - - (14)}$$

where T_l = fractional line transmittance

T_s = fractional transmittance at saturation

E = exposure

K = a constant incorporating the amount of the isotope in the sample and the sensitivity of the photoplate.

A correction must be made for the background exposure on the photoplate. The total exposure (in nanocoulombs) appearing on the photoplate is given by

$$E_{lb} = E_l + E_b \qquad \text{- - - - - - - - - - - - - - - - - (15)}$$

where E_{lb} = total exposure on photoplate

E_l = exposure due to the isotope

E_b = background exposure.

From equation 14

$$\frac{1 - T_1}{T_1 - T_s} = (KE)^R$$

$$\therefore \quad E = \frac{1}{K}\left[\frac{1 - T_1}{T_1 - T_s}\right]^{\frac{1}{R}} \text{ - - - - - - - - - - - - (16)}$$

Substitution of equation 16 and similar equations incorporating T_{1b} and T_b into equation 14 yields an equation for T_1 which has been corrected for background.

$$T_1 = \frac{1 + T_s\left[\left(\frac{1 - T_{1b}}{T_{1b} - T_s}\right)^{\frac{1}{R}} - \left(\frac{1 - T_b}{T_b - T_s}\right)^{\frac{1}{R}}\right]^R}{1 + \left[\left(\frac{1 - T_{1b}}{T_{1b} - T_s}\right)^{\frac{1}{R}} - \left(\frac{1 - T_b}{T_b - T_s}\right)^{\frac{1}{R}}\right]^R} \quad (17)$$

Similarly R may be evaluated by rearranging equation 16 for two data points. Here

$$R = \frac{\log\left[\left(\frac{1 - T_m}{T_m - T_s}\right)\left(\frac{T_n - T_s}{1 - T_n}\right)\right]}{\log\left[\frac{(aE)_m}{(aE)_n}\right]} \text{ - - - - - (18)}$$

where the subscripts m and n refer to two data points and 'a' is the isotopic abundance.

Clearly from equations 17 and 18 a iterative solution is called for to obtain an accurate estimate of R. However, Woolston[202] assumed R = 1 when calculating T_1 and then calculated a more accurate valve of R using equation 18. The factor K which incorporates both plate sensitivity and the amount of the isotope present was then calculated using equation 16 and the

accurate value of R. In addition, Woolston recommended that only R values in the range 0.75 - 1.25 should be accepted and if the calculated value fell outside these limits the appropriate limiting value was used in the calculation of K. Moreover, Woolston used a maximum of three exposures to determine the position of the transmission curve of any given isotope and it has been suggested by Franzen and Schuy[203] that three points are not enough to define the transmission curve accurately. In addition, the equation has been criticized because of its empirical nature and limited validity[203]. Grais[206] has examined the slope factor R in the Hull equation and has shown that for constant ion mass R is inversly proportional to ion energy.

There appears to be a certain amount of disagreement in the literature as to whether the photographic curve alters for differing mass numbers. Franzen and Schuy stated that their slope parameter v increases with decreasing ion mass and increasing ion energy, but did not know what the exact relationship was. Judson and Hull reported that R was nearly the same for all Ilford Q2 photoplates and was near to unity. Woolston has pointed out that Hull's slope parameter R was very sensitive to slight error in the data points and he found appreciable variation when R was calculated using different pairs of points for the same isotope. Therefore, Woolston has suggested that there is not enough evidence to show whether R varied according to isotopic mass or not. He concluded that it was better to take some average value of R and suggested that 1.0 was a good average value to choose. However, neither Woolston nor Judson and Hull stated which mass spectrometer they were using or the acceler-

ating voltage and because Grais has shown that R is dependent on ion energy the value of R chosen by Woolston may not be suitable for use with other mass spectrometers.

Therefore, there are three basic methods that may be used for the quantitation of the data obtained from photoplates. The first is the "minimum detectable line" method which is used extensively where only a rough estimate of impurity concentration is required. Secondly, there is a whole group of procedures which involve plotting the absorbance or a function of the absorbance of a line against the corresponding exposure. The procedure is repeated for each isotope under consideration and the exposure required to produce a given absorbance recorded. The procedure is somewhat subjective if performed graphically but some of the methods can be adapted for computer evaluation. The third basic technique is the genuine mathematical solution based on theoretically or empirically derived equations as described above.

In this thesis the "minimum detectable line" method was ignored as the method does not provide the necessary precision. The two remaining groups of methods are examined to find a procedure that produces good precision and is not subjective. In addition, the discrimination attainable between different glasses using mass spectrometry is investigated and glasses with unusual values of specific refractivity are examined.

10. APPARATUS

The mass spectrometer used in this study was an A.E.I. MS702 spark source mass spectrometer. The instrument features double focusing and the design is based on the geometry described by Mattauch and Hertzog.

Valves enable the source chamber to be isolated from the rest of the apparatus which remains under high vacuum while air is admitted into the source to facilitate sample changing. The sample electrodes in the form of rods 2-3mm in diameter are mounted in small chucks in the source which are connected to the high voltage supply. The samples may be moved whilst the source region is under vacuum by the use of remote handling devices (micromanipulators). Sparking conditions are adjusted by varying either the voltage of the pulsed r.f. discharge between 0 and 80Kv, the length of the pulse or the duration of the pulse. In addition, for very short exposures, facilities are available for ion beam chopping in which only a small portion of the ions produced by each pulse is allowed to reach the detector. The ions are accelerated in a potential of approximately 20Kv through a series of slits into the electrostatic analyser. This consists of a segment made up of two plates held at $\pm$1000v, which separate the ions according to energy. A given portion of the energy spectrum is admitted to the magnetic analyser for mass analysis while the remainder of the beam strikes the monitor collector which measures both the instantaneous ion current and the total amount of collected charge. There are 10 possible ranges of the magnetic analyser allowing mass range to be recorded of from 1 to 8 and from 8 to 280. Good vacuum is obtained by the use of 4 oil diffusion pumps backed by an oil rotary pump. The

diffusion pumps are spaced over the whole vacuum system. After admitting air to the source or photoplate magazine, each of these regions are pre-pumped down to about 0.1 torr before the valves are opened to connect these regions to the main pumping system. Pre-pumping is performed using the auxiliary vacuum system which consists of an untrapped rotary oil pump. The pressure in the analyser regions is maintained at 1×10^{-8} torr or better, but the pressure in the source region rises during sparking to around 5×10^{-5} torr. Cryosorption pumping is not used in the source chamber.

Photoplates are inserted into the instrument in light-tight cassettes which may be loaded 8 at a time into the photoplate magazine. The magazine is connected to the main pumping system so that the plates are thoroughly de-gassed before insertion into the magnetic analyser. The photoplates can be moved around the magazine and inserted into the magnetic section without breaking the vacuum by the use of remote handling devices.

The ion image is formed on the photoplate with the aid of a series of slits in the ion path and with various focusing controls. The two most important controls are the accelerating voltage which must be adjusted to give both good transmission and good resolution and the focus setting which alters the voltage applied to a slit at the entrance to the magnetic analyser (known as the Pim voltage). This control alters line shape only. The two controls are, to a certain extent, interdependent.

11. EXPERIMENTAL

11.1 SAMPLE PREPARATION

11.1.1. Cleaning

Samples for analysis on the mass spectrometer consisted of unused glass of recent manufacture or glass which had previously been cleaned for examination of its physical properties. In addition, each sample was degreased in re-distilled acetone for 5 minutes and then rinsed in deionized water. The sample was then allowed to stand for 10 minutes in concentrated nitric acid and then rinsed repeatedly in deionized water. The sample was finally dried under an infra-red lamp.

11.1.2. Grinding

The samples were ground in an agate mortar which had been cleaned in concentrated nitric acid, washed in deionized water and dried under an infra-red lamp. The use of paper tissues at any stage of the operation was avoided to prevent contamination of the sample with barium from the tissues[103]. The sample was placed in the mortar, together with about $5cm^3$ of re-distilled acetone. The acetone prevented the glass escaping from the mortar during the crushing operation. When the glass had been reduced to a small particle size crushing was continued in the dry state until the glass became a very fine powder. Finally the crushed glass was placed under an infra-red lamp for at least 20 minutes to remove all traces of the acetone. After cooling, the glass was transferred to a polythene stoppered glass vial for storage.

11.1.3. Mixing

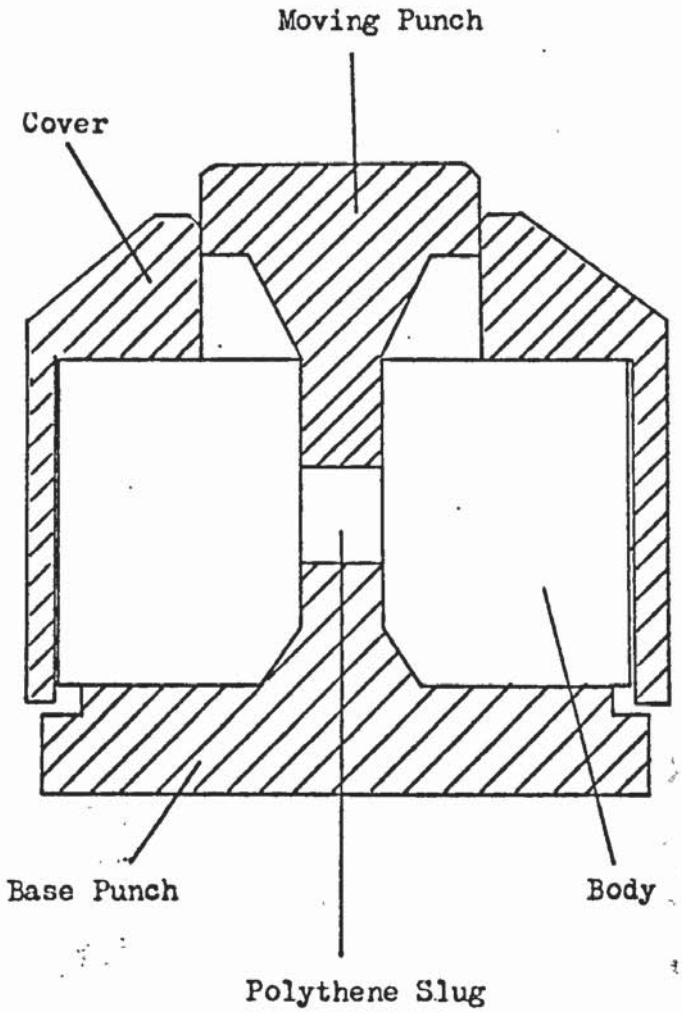
Depending on the quantity of glass available for use, different techniques were used for mixing the glass in with the matrix (almost invariably graphite). When only a small fragment of glass was available for analysis the crushed glass (1-2mg) was weighed on a Research and Industrial Instruments Company's electromicrobalance using a miniature scoop made from aluminium foil to hold the glass. The glass was then transferred to an agate vial which had been cleaned in the same manner as the agate mortar and pestle, together with a quantity of graphite (Ringsdorff RWA grade) equal in weight to that of the crushed glass. An agate ball was inserted in the vial followed by a tight fitting agate cap. The cap was held in position with sellotape and the vial was shaken in a Wig-l-Bug mixer (Crescent Dental Manufacturing Company, Chicargo, U.S.A.) for 20 minutes. If a large quantity of crushed glass was available 100mg was weighed out into a disposable polystyrene vial using a Mettler balance weighing to 0.00001g. The glass was then transferred to the agate vial and 100mg of graphite added to the crushed glass. The mixture was then shaken as before for 20 minutes.

If an internal standard was to be used it was added in the form of a standard mixture of graphite and lutetium oxide (Lu_2O_3) containing 1000ppm by weight of the latter. 20mg of the standard mixture was mixed with 80mg of graphite and 100mg of glass to give an internal standard concentration of 100ppm in the glass/graphite matrix.

11.1.4. Pelleting

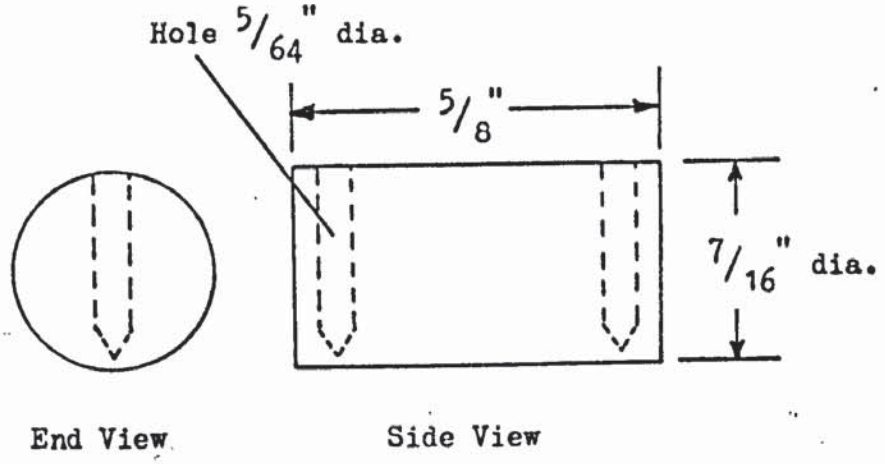
The A.E.I. pelleting die is shown in Figure 37. The polythene slugs in which the electrodes were formed were prepared by freezing the blank slugs in liquid nitrogen and then drilling 2 holes in each such that drill did not completely penetrate through the slug (Figure 38). Various drill sizes were used and a convenient size for the examination of glass was 5/64" diameter.

Tipped electrodes were normally used (Figure 39). These were prepared by transferring a small quantity of glass/graphite mixture to each of the holes in the slug and pressing it in firmly with a flat ended tungsten needle. In the case when only 3-4mg of glass/graphite mixture had been produced it was divided into two and half added to each cavity. The remaining part of the electrode was made from pure graphite which was not packed in as tightly to avoid difficulty in removing the electrode from the slug after pressing. The slug was inserted into the die which was pressed for 10 minutes at a pressure of 67 tons per square inch on the slug.



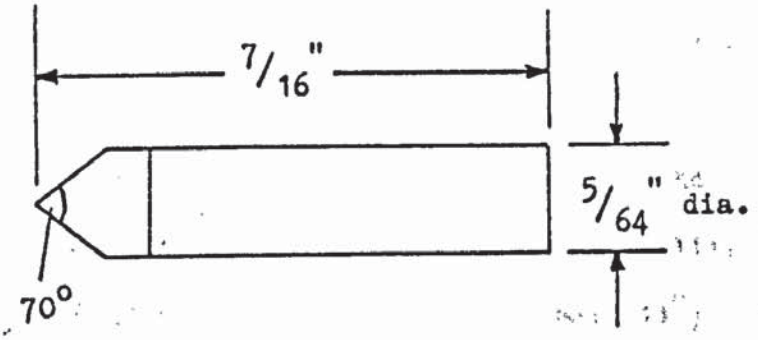
A.E.I. SAMPLE MOULDING DIE

FIG. 38



POLYTHENE MOULDING SLUG

FIG. 39



TIPPED ELECTRODE

11.2 SPARKING

The pressed electrode was carefully removed from the polythene slug and inserted into the sample holders located in the source of the instrument. Great care was exercised to ensure that the clamps were not over tightened thereby crushing the electrode.

For good precision the distance between the first slit and the electrodes was found to be of critical importance, and it was essential that this distance was the same for each pair of electrodes. A perspex jig was used incorporating a prong which rested against the first slit plate 3-4mm above the electrodes. A mark was made on the prong 7mm from the end touching the slit plate. Three to four millimeters below the electrodes another prong protruded from the jig to within 7mm of the slit plate. A mirror was held at 45° above the top prong and by slight adjustment of the mirror it was possible to align the two prongs. The electrodes were adjusted so that they were exactly 7mm from the first slit.

A travelling microscope was used to ensure that the electrodes were positioned directly in front of the first slit. The axis of the mass spectrometer is angled at 0.192rad (11°) to the horizontal. In these experiments the microscope was inclined at the same angle. The interior of the source and the slits were illuminated by 4 low voltage lamps held in a clip around the periphery of the microscope objective. The microscope was focused on the second slit and the intersection of the cross wires in the microscope eyepiece was brought to the centre of the slit using the adjusters on the microscope. The microscope was

then racked backwards until the electrodes were in focus and, using the micromanipulators, the two electrodes were adjusted until they were level and almost touching, each being equidistant from the vertical cross wire. The eyepiece with the cross wires was then replaced with an eyepiece which had a graticule in the horizontal axis. The electrodes were adjusted until they were 0.1mm from the centre line of the graticule.

The glass face-plate was placed on the source chamber and the source pumped down to approximately 1×10^{-6} torr. The sparking conditions were 25% of total spark voltage, pulse length 200μs, pulse rate 300 pulses s^{-1} and magnet range 10 (313mA) giving a mass coverage of 8 to 280 mass units. Fourteen exposures were made on each plate, but the exposure range was restricted to 0.1nC - 20nC to improve precision. Each pair of electrodes were given a 15nC pre-spark before the exposures on the photoplate were made. Throughout the duration of sparking the gap between the electrodes was maintained constant by periodic adjustment of the electrodes.

After exposure the photoplates were developed, 2 at a time, in Ilford Caustic Hydroquinone developer for 2.5 minutes at 20°C, using constant agitation by hand. The plates were washed in running water at 20°C for 30 seconds and then fixed in May and Baker Amfix for 90 seconds. The plates were given a final wash in running water for 5 minutes followed by 15 seconds in a wetting agent. The plates were dried in a film drying cabinet.

The analysis of glass by spark source mass spectrometry has been developed by Scaplehorn and is described elsewhere[216].

11.3 PHOTOPLATE READING

Before each plate was examined using the microdensitometer it was inspected to detect any outstanding features of the analysis and to decide which isotopes would be measured accurately on the microdensitometer. In addition, a check was made for instrument faults in the mass spectrometer, e.g. loss of resolution.

The instrument used to read the photoplates was a Joyce Loebl Mk.III cs recording microdensitometer which produces a graph of photoplate darkening vs. position on the plate. The trace produced is linear in absorbance and the range covered can be altered by changing the reference wedge in the instrument.

The microdensitometer was calibrated using Kodak neutral density filters of known absorbance. The optical system of the instrument was brought into focus and a baseline established with no filter in the light path. The filter was brought into the light path and the instrument refocused. With filters of low absorbance it was possible to refocus visually, but with the denser filters it was necessary to focus by observing the amount of pen deflection. When the pen deflection was at a minimum, the instrument was correctly focused. A short trace was drawn on the chart paper to record the absorbance of that filter. This procedure was followed for all other filters in the range of interest. The distance on the chart from the baseline to each trace was measured and a calibration graph constructed of pen deflection (in mm) against the known absorbance of the filter. The best straight line was fitted through the points using the method of least squares and the deflection equal to an absorbance

of 1.0 calculated. The calibration was repeated at weekly intervals, but the total range of results obtained over a period of several months was less than 0.5% indicating extremely good stability.

Correct plate alignment was an important factor when reading photoplates. This was accomplished by adjusting the controls on the photoplate carriage such that each line being examined was parallel to the slits in the instrument. Failure to do this produced broad peaks with reduced peak height. The alignment of the photoplate was checked and adjusted as necessary for each isotope examined.

The correct focusing of each spectrographic line was found to be important. This was achieved by bringing one of the lines into the light path and adjusting the focus control to give maximum deflection.

In early experiments zero absorbance was taken from a photoplate which had been fixed, but not developed[213]. All measurements of line density on the photoplates were made with reference to this zero line. This method had the advantage that the absorbance was always measured from the same reference line and that the varying background on the photoplate was always taken into account.

The distance from the baseline to the base of the peak (H_b) and the distance from the baseline to the top of the peak (H_{1b}) was measured from the microdensitometer trace. In later experiments only the height of the peak from its base to apex was measured (H_1).

11.4 THE TECHNIQUES AVAILABLE FOR THE INTERPRETATION OF DATA

11.4.1. A Simple Graphical Method

Many workers have used a simple graphical procedure to improve the precision of the results. The method followed in this laboratory involved plotting the exposure (log scale) against the absorbance and because this method was used exclusively before mathematical techniques were investigated, it was used as a reference method to which other procedures were compared. A typical graph is shown in Figure 40, each isotope producing its own curve. From this it is clear that the points lying in the central portion of the curve are in a straight line and providing that the emulsion response is the same for ions of all masses, then the central portion of these curves should be parallel. It was found experimentally that if all lines were drawn parallel to each other then better precision was obtained than if the slope was chosen individually for each isotope. When all the lines were drawn parallel the slope of the lines for each plate was determined by assessing the slopes of 3 or 4 lines and using the approximate average.

Generally either calcium, manganese or lutetium was used as an internal standard and the absorbance which was equivalent to an exposure of 1nC was determined.

The exposure necessary to give this absorbance for each of the other isotopes was then determined and the result expressed as a ratio of the exposures of the standard to the unknown. This procedure was found to be adequate for comparative purposes.

A SIMPLE GRAPHICAL METHOD SHOWING A PLOT OF LOG EXPOSURE AGAINST PEAK HEIGHT FOR TWO ISOTOPES

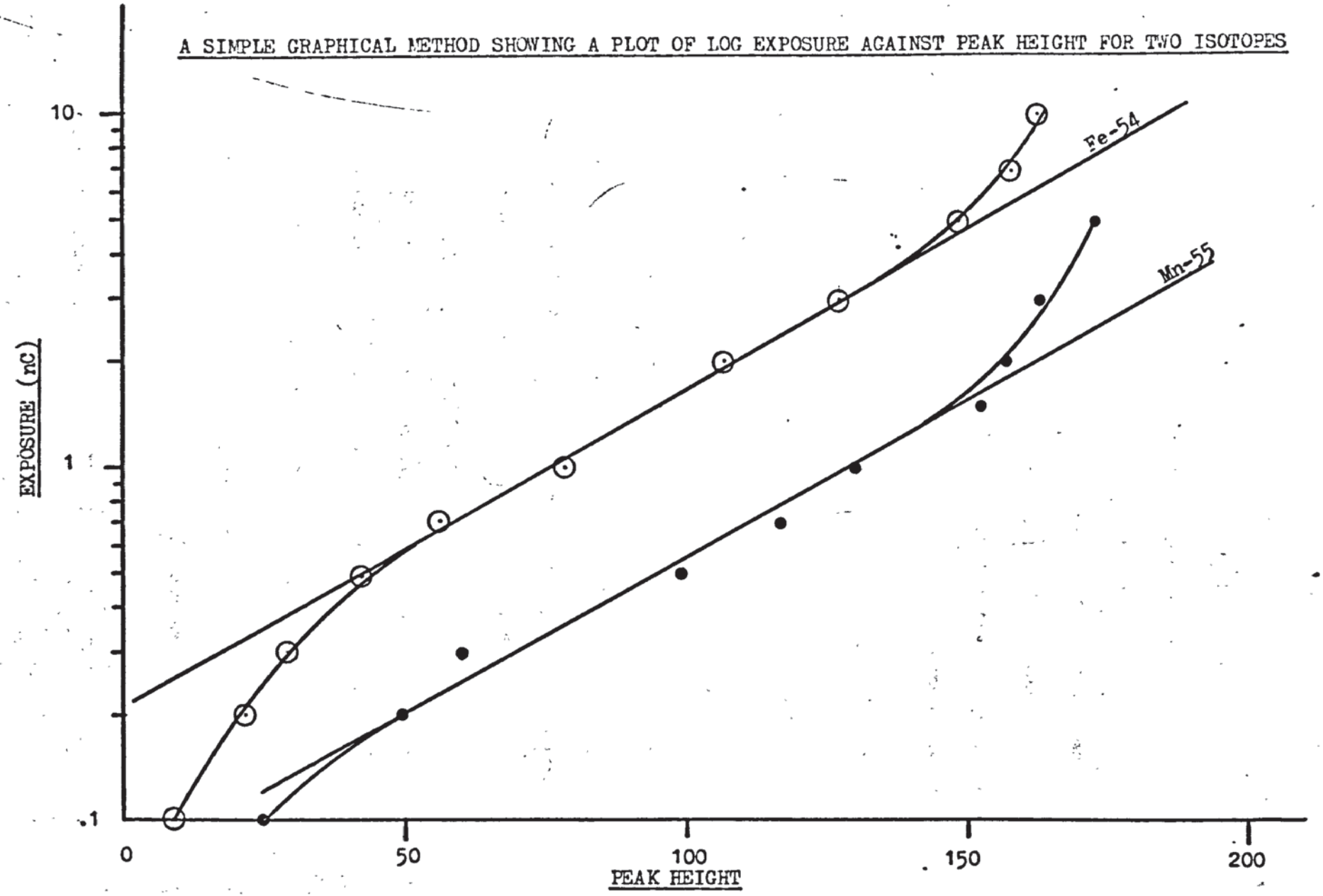


FIG. 40

11.4.2. Wagner Method

The log(absorbance) was plotted against log(exposure) as shown in Figure 41. The correction for background was made by using equation 1 (Section 9). The points were plotted manually and the best straight line drawn through the points at an angle of 45° to the axis. The position of the line was determined subjectively by an examination of the position of the points. The exposures necessary to obtain a given absorbance were then read off for each isotope and the exposure ratio to the standard calculated. The algorithm was also solved by computer. The points on the straight portion of the curve were indexed into the computer (Hewlett-Packard 9100B) which was programmed to perform a least squares fit assuming the slope to be unity. The exposure necessary to give a certain absorbance was calculated for each isotope and the ratio to the standard determined. Table 22 shows the precision obtained with the manual and computer procedure. Wagner plots for two different isotopes from two different batches of photoplates are shown in Figure 41.

11.4.3 Seidel Linearization

The absorbance of the lines on a photoplate were converted to the Seidel function (Δ) using the equation

$$\Delta = \log\left(\frac{1}{T} - 1\right) \qquad (19)$$

where T = fractional transmittance.

The correction for background was carried out using equation 1. A plot of Δ vs. log E for isotope lines on two different plates is shown in Figure 42.

FIG. 41

WAGNER PLOT SHOWING GRAPHS FOR TWO ISOTOPES

RECORDED ON TWO DIFFERENT PLATES

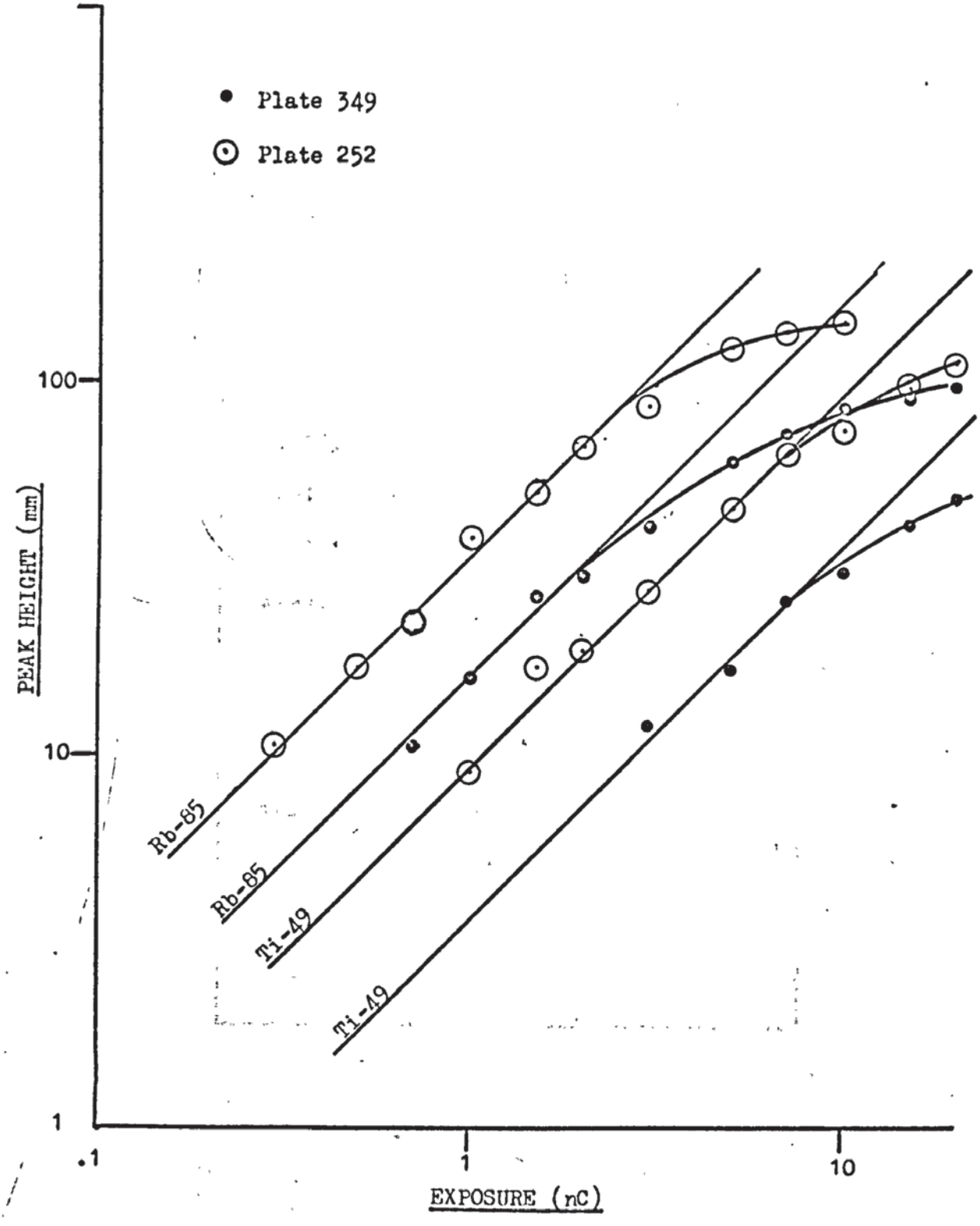
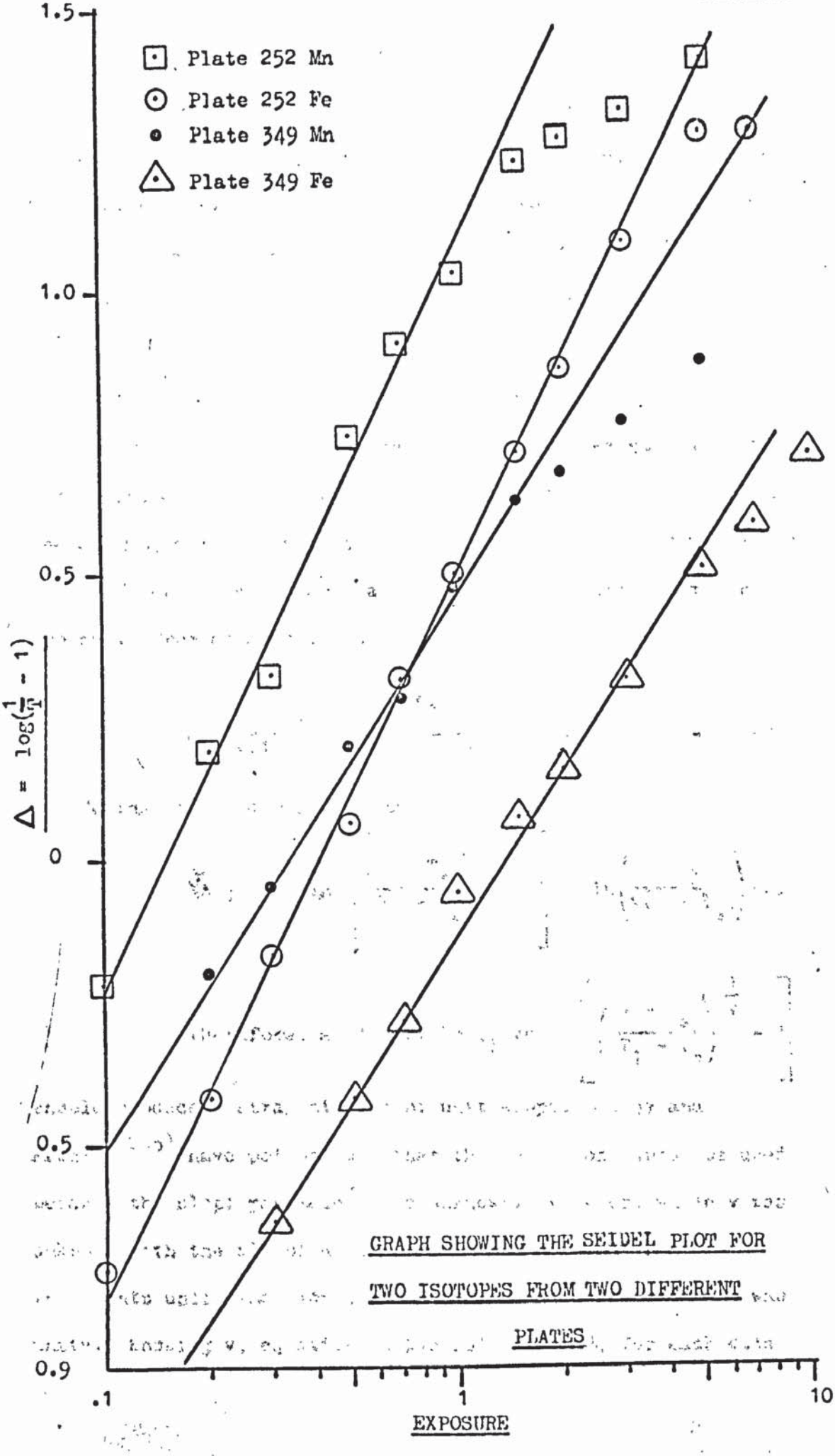


TABLE 22

Wagner Plot. Plates 1-4. Comparison of the precision between manual and computer procedures.

	Coefficient of Variation %	
	Manual Plotting	Computer Plot
Lu-175	-	-
Ba-138	4	5
Ba-137	2	1
Zr-90	10	8
Sr-86	5	8
Rb-85	11	9
Mn-55	9	18
Fe-54	11	10
Ti-49	14	10
Mean	8	9

FIG. 42



GRAPH SHOWING THE SEIDEL PLOT FOR TWO ISOTOPES FROM TWO DIFFERENT PLATES

11.4.4. Kaiser Linearization

This equation was investigated for use with the ion-produced images obtained in mass spectrometry, but initial experiments showed that this equation caused more deviation from linearity than the Seidel function. Figure 43 shows a graph of log E vs. K for one isotope using different values of f. (see Section 9 equation 2).

11.4.5. The Equation of Franzen and Schuy

(a) Linearization. Because the Hewlett-Packard desk computer used in this study had less storage capacity than the Siemens computer used by Franzen and Schuy, it was necessary to try to obtain a linear transmission curve which is easier to process. From equations 8 and 12

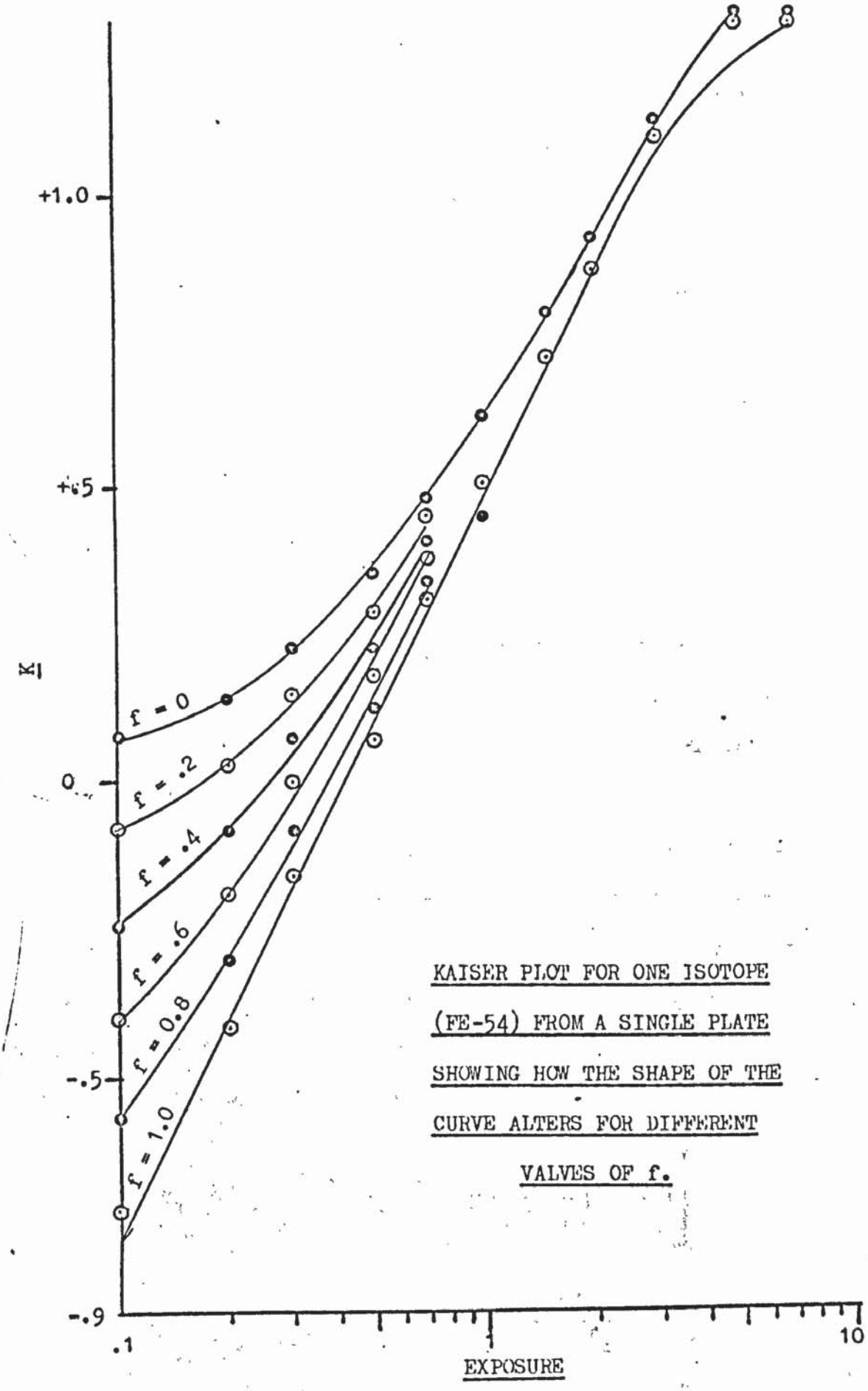
$$q_1 \cdot \frac{P_1}{v(1 - T_s)} = \left(\frac{1 - T_s}{T_1 - T_s}\right)^{\frac{1}{v}} - 1 \quad \text{------} \quad (20)$$

Taking logs and rearranging

$$\ln q_1 = \ln \left[\left(\frac{1 - T_s}{T_1 - T_s}\right)^{\frac{1}{v}} - 1\right] - \ln\left(\frac{P_1}{v(1 - T_s)}\right) \quad (21)$$

Therefore, a plot of $\ln q_1$ vs $\ln \left[\left(\frac{1 - T_s}{T_1 - T_s}\right)^{\frac{1}{v}} - 1\right]$ should produce a straight line of unit slope. Schuy and Franzen[205] have pointed out that this equation cannot be used because the slope parameter v is unknown. However, while v was unknown with the aid of a computer it was altered in stepwise increments until the slope, calculated using least squares, was unity. Knowing v, equation 13 was solved for P_1 for each data

FIG. 43



KAISER PLOT FOR ONE ISOTOPE (FE-54) FROM A SINGLE PLATE SHOWING HOW THE SHAPE OF THE CURVE ALTERS FOR DIFFERENT VALVES OF f.

point. All the values for P_1 for a given isotope were then averaged geometrically and the relative concentrations between isotopes on a given plate was calculated by forming a ratio between the values of P_1 for the standard and the unknown. The absolute photographic sensitivity and the relative sensitivity cancelled out leaving a ratio dependent on concentrations only. A flow chart showing the essential steps in the computer programme used to calculate v, together with the programme (for a Hewlett-Packard 9100B) is given in Appendix 3.

Table 23 shows the precisions obtained on a series of photoplates using the linearized Franzen equation and using the value of the slope parameter v calculated for each individual line.

Table 24 shows the precision obtained when an approximate background correction is made and v is varied in a linear manner over the photoplate. The reasons for using this approach are discussed later.

(b) Differential Method. It has been pointed out by Page[217] that possibly a more elegant method of determining the slope parameter v in the equation of Franzen and Schuy, is to calculate it using differential calculus rather than 'guessing it' as was used in the previous method.

From equations 9 and 13

$$P_1 = \frac{b\ l\ v\ (1 - T_s)}{e_{rel}\ \varepsilon\ h\ E}\left[\left(\frac{1 - T_s}{T_1 - T_s}\right)^{\frac{1}{v}} - 1\right]$$

Let $\frac{b\ l}{e_{rel}\ \varepsilon\ h} = A$ and let $\frac{1 - T_s}{T_1 - T_s} = B$

TABLE 23

Precision obtained using the Franzen equation for plates 5-8. The ratios of P_1 were determined from values of v calculated individually for each isotope. All results are expressed as a ratio to Mn-55.

	Unweighted		
	Mean	Standard Deviation	Coefficient of Variation %
Lu-175	.217	.079	36
Ba-138	.506	.108	21
Ba-137	.511	.086	17
Zr-90	.118	.023	20
Sr-86	.201	.021	11
Rb-85	.537	.109	20
Mn-55	1.0	-	-
Fe-54	6.03	1.35	22
Ti-49	1.66	.17	10
Ca-43	731	247	34
		Mean	21

TABLE 24

Plates 5-8. Background corrected by $A_l = A_{lb} - A_b$. v was calculated using the incremental technique and a linear relationship assumed between v and mass. Isotopic abundance was taken into account and all P_l values are expressed as a ratio to manganese.

	Mean P_l	Coefficient of Variation %
Lu-175	.200	15
Ba-138	.504	15
Ba-137	.471	11
Zr-90	.120	6
Sr-86	.220	5
Rb-85	.553	6
Mn-55	1.0	-
Fe-54	6.016	8
Ti-49	1.395	21
Ca-43	588.	10
Mean		11

Substituting and rearranging yields

$$\frac{E}{1 - T_s} = \frac{AVB}{P_1}^{\frac{1}{v}} - \frac{AV}{P_1}$$

Differentiating $\frac{E}{1 - T_s}$ with respect to B yields

$$\frac{d\left(\frac{E}{1 - T_s}\right)}{dB} = \frac{A}{P_1} \cdot B^{\left(\frac{1}{v} - 1\right)}$$

Taking logs

$$\ln\left[\frac{d\left(\frac{E}{1 - T_s}\right)}{dB}\right] = \left(\frac{1}{v} - 1\right) \ln B + \ln \frac{A}{P_1}$$

A plot of $\frac{E}{1 - T_s}$ vs $\frac{1 - T_s}{T_1 - T_s}$ was prepared and its slope measured at a number of points. The log of the slope was then plotted against $\ln\left(\frac{1 - T_s}{T_1 - T_s}\right)$ and v calculated.

In order that the complete calculation could be carried out on the computer it was assumed that the points on the graph of $\frac{E}{1 - T_s}$ vs $\frac{1 - T_s}{T_1 - T_s}$ were connected by a series of straight lines. The results showed a coefficient of variation of around 40%.

11.4.6. The Hull Equation

A set of four plates were examined using Woolston's method of interpretation and using a maximum of 3 data points. T_1 was calculated using equation 17 assuming R = 1. A more accurate value of R was then calculated using equation 18 and if

more than two data points were available R was calculated for all possible combinations and the result averaged arithmetically. The factor K was then calculated for each exposure using equation 16 and the results averaged geometrically. Because the primary requirement of this work was to compare the results obtained on two glass samples, isotopic abundance was not taken into account. In addition, line width differences were ignored. The results are given in Table 25 under the heading 'Woolston's Method'.

11.4.7. Linearized Hull Equation

The Hull equation (equation 14) may readily be linearized to give an equation in the form $y = mx + c$.

From equation 16, taking logs and rearranging

$$\ln E = \frac{1}{R} \ln \left(\frac{1 - T_1}{T_1 - T_s} \right) - \ln K \text{ - - - - - - -(22)}$$

Therefore, a plot of $\ln E$ vs $\ln \left(\frac{1 - T_1}{T_1 - T_s} \right)$ should yield a straight line of slope $\frac{1}{R}$.

The data from the set of photoplates previously examined were re-processed using the linearized Hull equation. In this case more data points (typically 7) were used for each isotope and T_1 was calculated using equation 17 with an assumed value of R (generally 1.0). A better value of R was then calculated from the T_1 values using equation 22 and hence a more accurate value of K. The data points were fitted to equation 22 using the method of least squares. The better value of R was then used to obtain a better set of T_1 values and the process

TABLE 25

Coefficients of Variation obtained using the Hull equation. Plates 5-8. Comparison of Woolston's method with a linearization technique. All results are given as a ratio to Mn-55.

	Coefficient of Variation %		
Method / Isotope	Woolston's	'A' (Linearized)	Simple Graphical
Lu-175	52	14	9
Ba-138	48	20	12
Ba-137	56	15	10
Zr-90	51	13	7
Sr-86	23	9	6
Rb-85	23	11	5
Mn-55	-	-	-
Fe-54	44	20	7
Ti-49	48	17	10
Ca-43	46	10	6
Mean	43	14	8

was repeated until the change in K was less than 1%.

On each iteration all the data points had to be indexed into the computer again and, therefore, the method was rather time consuming. The precision obtained using this technique is shown in Table 25 under the heading of method 'A'.

Because the photoplates were exposed under carefully controlled sparking conditions and the maximum exposure was limited to 20nC, the amount of background fog on the photoplate was small. Moreover, the variation in background between the highest and lowest exposures was generally small, except for calcium 43 where the background on the longer exposures was measurably greater than on the shorter exposures. Because the background was fairly even it was possible to use the same background correction procedure described in Section 9 dealing with the Wagner equation and because the microdensitometer was calibrated in absorbance, the peak height above background could be read directly from the microdensitometer trace. It was important that the absorbance at saturation (A_s) was determined in the same manner as the other absorbances, i.e. absorbance above background. Failure to do this resulted in curvature of the graphs as saturation was approached.

The data from a series of photoplates was processed using the above method for background correction. The exposure and absorbance were indexed into the computer (Hewlett-Packard 9100B) and a least squares programme was used to find the best fit for the data points using equation 22. Thus a value of the slope factor R was calculated for each mass number which had 6 or more data points.

Because of the uncertainty as to how R varied it was assumed that there was a linear relationship between the value of R and the mass number. For each isotope with six or more pairs of data points below saturation the values were indexed into the computer and the value of R calculated for each isotope. The method of least squares was then used to find the best fit of the points assuming a linear relationship between R and the mass number. A corrected value of R ($R_{corrected}$) was then calculated for each isotope from the calculated relationship between R and mass number. $R_{corrected}$ was then used to calculate the value of K for each pair of data points using equation 16. The ratio of the values of K between the standard (manganese) and unknown were calculated and the precision obtained using this procedure is given in Table 26.

It is conventional to estimate the concentration of a given isotope by determining its ratio to an internal standard of known concentration. This standard can either be added to the glass/graphite mixture or be an element that is present in the glass and whose concentration has been determined by some independent method. The procedure of calculating the ratio to an internal standard has the disadvantage that any lack of precision in the standard is reflected in the precisions of all the other elements, in addition to the error associated with the elements themselves.

An alternative approach, as used with electrical detection, is to calculate the ratio of each isotope to the total ion beam falling on the photoplate. Such an approach would involve measuring every line appearing on the photoplate and is, there-

TABLE 26

Precision obtained using the Hull equation with Plates 5-8. R was altered with mass assuming a linear relationship. The isotopic abundance was assumed to be 1 in each case.

Isotope	Coefficient of Variation %		
	Ratio to Mn	Ratio to total ion beam	Simple Graphical. Ratio to Mn.
Lu-175	14	-	9
Ba-138	14	12	12
Ba-137	10	9	10
Zr-90	6	3	7
Sr-86	7	6	6
Rb-85	4	3	5
Mn-55	-	4	-
Fe-54	6	4	7
Ti-49	8	6	10
Ca-43	7	6	6
Mean	8	6	8

fore, not feasible due to the large amount of work involved. However, the same principle can be followed if a fixed set of elements are chosen which are measured on every plate. In this procedure the K values of each element on a given plate were summed to give K_{tot}. Each individual value of K was then divided by K_{tot} and multiplied by 100 to yield an answer in percent. This percentage figure can be regarded as a percentage of the ion beam for the isotopes measured.

A flow chart describing the computer programme used to calculate R is given in Appendix 4, together with the computer programmes (for a Hewlett-Packard 9100B) used to calculate R and K_{tot}. Table 26 shows the precision obtained when R was varied linearly over the plate and when the K values were expressed as a ratio to K_{tot}.

Experience obtained in the examination of about eighty photoplates indicated that the variation in R over the photoplate was generally small. Typically the change in R was equivalent to only about a $3\text{-}5^{\circ}$ change in slope. Therefore, because the variation in R was small, the results from one set of photoplates was calculated with R varying as normal and again with R being held constant over the plate. The results are shown in Table 27.

TABLE 27

Precision obtained using the Hull equation on Plates 9-12. The isotope concentrations are expressed as a ratio to total ion beam of isotopes measured.

Isotope	Coefficient of Variation %	
	R varying	R constant
Ce-140	7.8	10.2
La-139	10.6	13.7
Ba-138	14.9	14.0
Ba-137	9.4	10.2
Zr-90	2.7	4.1
Sr-86	10.8	11.5
Rb-85	9.3	9.9
As-75	29.7	31.1
Co-59	19.7	20.4
Mn-55	7.6	6.5
Fe-54	18.0	16.7
V-51	9.6	9.6
Ti-49	9.2	8.3
Ca-43	7.4	6.6
Mean	11.9	12.3

11.5 INVESTIGATION OF GLASSES WITH UNUSUAL SPECIFIC REFRACTIVITIES

During the survey of glasses from the Scenes of Fires described in Section 6.1, three glasses were encountered which had values of specific refractivity (k) which were well removed from the average value obtained for all the glasses. The composition of the glasses was investigated using the mass spectrometer to try to establish the reason for these large variations in the value of k.

The procedure of sample preparations and sparking was exactly the same as that described in Section 11. The data obtained from the photoplates was interpreted using the linearized Hull equation and all the values of k were calculated as a ratio to Ca-43 which acted as an internal standard. The concentrations relative to Ca-43 obtained for the three glasses are shown in Table 28, together with the results obtained from a standard glass of known composition supplied by Pilkington Brothers.

These results are considered in Section 12.7.

TABLE 28

Analytical results obtained for glasses with unusual specific refractivities. The results are expressed as a ratio to Ca-43 and sensitivity factors are not taken into account.

Parameter \ Sample No.	83	692	927	CL 17G*
R.I.	1.5115	1.5305	1.5231	1.5158
DENSITY(g cm^{-3})	2.4766	2.6628	2.5314	2.4832
k	0.121062	0.116097	0.120696	0.121595
Pb-208	ND	0.0367	ND	ND
Ba-138	0.0841	46.3	54.0	0.325
Ba-137	0.0133	25.6	8.87	0.040
Ba-134	ND	7.74	1.94	ND
Sn-118	ND	ND	.0346	ND
Zr-90	0.0781	0.0593	.0558	0.0569
Sr-86	0.0138	1.05	0.121	0.0228
Rb-85	0.309	0.160	0.0151	0.284
As-75	ND	6.88	0.0103	ND
Co-59	2.33	3.52	0.0140	ND
Fe-56	ND	ND	0.536	ND
Mn-55	0.662	0.187	0.0097	0.954
Fe-54	0.581	0.231	0.0254	0.368
V-51	0.0279	0.0359	0.00621	0.0303
Ti-49	0.122	0.0853	0.0384	0.0778
Ca-43	1.0	1.0	1.0	1.0
K-41	11.8	6.60	3.7	12.6
Si-30	84.1	28.8	39.9	76.2
Al-27	91.4	47.7	24.6	51.4
Mg-26	57.3	0.290	0.094	33.0

N.D. = not detected in measurable quantities.

*CL 17G Standard glass supplied by Pilkington Brothers.

12. DISCUSSION OF THE VARIOUS MATHEMATICAL TECHNIQUES

12.1 A SIMPLE GRAPHICAL METHOD

With this method the analyst who is plotting the data points has a number of decisions to make which could lead to argument should the results become evidence in a prosecution brought by the police. From Figure 40 it is clear that only the points lying on the straight portion of the curve should be considered and it is sometimes difficult to determine whether a point is in fact lying in the linear portion of the curve. In addition, the operator has to decide both the vertical position and the slope of the line that is drawn through the points. However, the slope of the line for a given set of points may be estimated in conjunction with the points obtained for other isotopes. The situation is complicated by the fact that sometimes the lines for different isotopes are clearly not parallel. The reasons for these atypical results are not clear, but are most likely to be due to either sample heterogeneity, variations in the spark plasma or local imperfections in the photoplate.

The advantage of using a simple graphical method (or indeed, any graphical method) is that spurious results are easily detected and excluded from subsequent calculations, thereby increasing the precision.

12.2 WAGNER METHOD

When performed graphically the Wagner method has the same disadvantages as the simple graphical method, except that the slope is already pre-set to unity. The use of a computer removes much of the subjectivity of the method, but problems arise in determining the point at which the curve deviates from unit slope. Examination of Figure 41 shows that this point varies from plate to plate and is also dependent on developing conditions. For use on a routine basis it would, therefore, be necessary to plot the line of at least one isotope from each plate in order to determine the point at which the slope deviated from linearity. However, the method does provide a very simple and straightforward computer interpretation of a mass spectrum. In addition, because the slope of the curve is known, it is possible to estimate the concentration of an isotope from a single exposure.

Table 22 shows that an average coefficient of variation of 8% was obtained by manual plotting and 9% for computer evaluation. These are quite good results when compared with the precisions reported with other techniques and would be adequate for the purpose of the comparison of glass fragments if it were not for the subjectivity which is inherent in the method.

12.3 SEIDEL LINEARIZATION

Figure 42 shows that the Seidel linearization gives a greater range of exposures over which a straight line may be obtained than either the Wagner or the simple graphical method. However, the method has a number of disadvantages. One of these is that Δ (See Section 11.4.3.) must be calculated before it can be plotted, whereas the parameters in the simple graphical method and the Wagner method do not need calculating. In addition, the length of the linear section varies according to photoplate sensitivity and the slopes of each line must be determined in each case. Therefore, the Seidel Linearization offers no distinct advantages over the two preceding methods and possesses additional disadvantages. For these reasons no further work was carried out using this technique.

12.4 KAISER LINEARIZATION

This method of interpretation is clearly unsuitable for ion produced images. When f is unity the Kaiser function K (equation 2) reduces to the Seidel function and when f is equal to zero K reduces to the simple graphical method. Because the Kaiser linearization does not take the transmission at emulsion saturation into account, the method only affects the bottom part of the curve log E vs. K., that is, for low exposures and fails to influence the high exposure end of the curve. This result would be expected from the knowledge that the Kaiser linearization is a combination of the Seidel and simple graphical methods of interpretation. With both the latter methods the curve deviates from linearity at the high exposure end, and therefore, the Kaiser function suffered from the disadvantages of both the conventional method and the Seidel method and because of this, the technique was not investigated further.

12.5 THE EQUATION OF FRANZEN AND SCHUY

This method of photoplate interpretation gave disappointing results in the first instance (Table 23) when the correction for background was made using the equation recommended by Franzen and Schuy (equation 4). However, when an approximate background correction was applied and v was assumed to vary over the photoplate in a linear manner, the precision increased from 21% to 11% (Tables 23 and 24), but did not produce such a good precision as the simple graphical method. In addition, it took a relatively long time to calculate v on the computer.

The differential method provided an alternative means of calculating the slope parameter v in Franzen and Schuy's equation. To obtain the best results from the differential method it was necessary to plot the graph of $\frac{E}{1 - T_s}$ vs $\frac{1 - T_s}{T_1 - T_s}$ manually and to apply a certain amount of smoothing before the slope was determined. The process was time consuming because the procedure had to be repeated for each isotope. Because the graph of $\frac{E}{1 - T_s}$ vs $\frac{1 - T_s}{T_1 - T_s}$ had to be plotted manually and could not be dealt with on the small computer available, the method does not fulfil the criteria regarding objectivity as laid down in Section 1. Instead of plotting the graph manually it was possible to arrive at an approximate solution by assuming that all the points on the curve of $\frac{E}{1 - T_s}$ vs $\frac{1 - T_s}{T_1 - T_s}$ were connected by a series of straight lines. The disadvantage of the latter procedure was that it could lead to errors if one or two points were suspect and the results obtained showed that the procedure

lacked precision.

Goshgarian and Jensen[166] have carried out a preliminary investigation of the equation of Franzen and Schuy and reported disappointing results. However, they did not describe which technique they used to calculate v. The results obtained using the Franzen and Schuy equation in this study led to conclusions which were in agreement with those of Goshgarian and Jensen.

12.6 THE HULL EQUATION

The initial investigation using Woolston's approach produced results with a coefficient of variation of approximately 43% which is very poor. However, the use of a linearized version of the Hull equation increased the precision to about 14%. Table 26 shows that it was again possible to use an approximate correction for background and yet still obtain a precision as high as 6%.

The variation in R over the photoplate was found to be small after examination of a large number of photoplates and for the experimental conditions described in this study it could probably be assumed to be constant.

In Section 9 it was reported that Paulsen obtained a linear relationship if he plotted

$$\log E \quad \text{vs} \quad \log\left[\frac{1}{1 - \kappa/\kappa_s} - 1\right]$$

The intrinsic equation is, therefore,

$$\log E = m \log\left[\frac{1}{1 - \kappa/\kappa_s} - 1\right] - \log C.$$

where m = slope

c = constant

If T = fractional transmittance then

$\kappa = 1 - T$

$$\text{and } \log E = m \log\left[\frac{1 - T_s}{T - T_s} - 1\right] - \log C$$

Removing logs and rearranging

$$EC = \left[\frac{1 - T_s}{T - T_s} - 1\right]^m$$

and by taking roots and rearranging

$$\frac{T - T_s}{1 - T} = \frac{1}{1 + (EC)^{\frac{1}{m}}}$$

This equation is the same as the one proposed by Hull where C = Hull's K and $\frac{1}{m}$ = Hull's R. Thus Paulsen's approach is the same as Hull's.

The use of the Hull equation produced a coefficient of variation as low as 6%, but was more typically around 10%. However, a precision of 10% was at least as good as any of the other mathematical techniques investigated for the interpretation of mass spectrometric photoplates. In addition, it was an objective in the approach to the interpretation of the results and the necessary calculations were easily and quickly executed on the desk computer. Therefore, it was clearly the method of choice to use in subsequent investigations.

12.7 GLASSES WITH UNUSUAL SPECIFIC REFRACTIVITIES

Examination of the analytical results in Table 28 shows that the three glasses are certainly different to each other and moreover are very different to modern glass. This is the result which would be expected from an examination of the refractive index, density and specific refractivity, but the magnitude of some of the differences is surprising. The important factor is the wide variation in the concentration of the major constituents (potassium, silicon, aluminium and magnesium). The absence of appreciable amounts of magnesium in samples 692 and 927 suggest that these glasses are fairly old. As regards the 'trace elements' samples 692 and 927 are notable for their high barium concentration which is of the same order as the concentration of aluminium. Samples 83 and 692 contain a relatively large amount of cobalt and sample 692 also has a high concentration of arsenic. However, the real differences are apparent in the major constituents and it is clear from this study that it is highly probable that glasses possessing unusual values of specific refractivity do, in fact, have grossly different major constituents.

These findings are supported by the work of Coleman et al who have analysed glass using neutron activation analysis.

Table 29 shows the analytical results obtained for the major constituents, together with the values of refractive index, density and specific refractivity. It is clear from this table that in many cases changes in major composition are accompanied by a change in specific refractivity.

TABLE 29

Analytical results obtained on glasses from the Fire Survey obtained by Coleman et al using Neutron Activation Analysis

Parameter \ Samples	21	37	41	10	25	39	6	42
R.I.	1.5286	1.5285	1.5285	1.5175	1.5176	1.5176	1.5168	1.5167
Density(g cm^{-3})	2.5340	2.5302	2.5273	2.4909	2.4896	2.4820	2.5243	2.4864
k	0.121632	0.121796	0.121936	0.121555	0.121638	0.121521	0.119891	0.121621
Al(%)	0.66	0.29	0.31	0.71	0.49	0.70	0.31	0.73
Ca(%)	8.24	12.5	10.93	10.44	7.11	6.95	10.68	7.29
Na(%)	9.44	8.51	9.38	10.36	9.60	10.07	8.32	8.84
Mg(%)	0.55	N.D.	1.88	1.93	2.01	1.93	0.42	3.90

13. DISCRIMINATION ATTAINABLE USING MASS SPECTROMETRY

To determine the usefulness of mass spectrometry as an analytical technique for the forensic examination of glass, four main areas must be investigated. They are:-

(a) The variation in composition between glasses of the same refractive index and density.

(b) The variation in composition between factories.

(c) The variation in glass composition within one factory.

(d) The difference in results obtained when different operators examine the same glass on the same mass spectrometer.

Clearly item (a) is the most important because it is a measure of the increased discrimination obtainable over and above that obtained using current techniques involving the use of refractive index and density. Item (b) would enable the glass to be assigned to a particular manufacturing site and would facilitate the identification of imported glasses. As regards forensic science the wider the variation within one factory the better as this will enable the glasses to be separated into a larger number of groups. However, the results from item (c) may be of limited value because previous experience has shown that although a day-to-day variation could be detected in both the physical properties and the iron content of glass, the variation tended to oscillate between fairly close limits, and therefore, it is a matter of chance whether it is possible to distinguish between glass produced on two given days.

13.1 EXPERIMENTAL

The glasses selected for the four different experiments were prepared and sparked as described in Section 11. Photoplate interpretation was carried out using the linearized Hull equation (Section 11.4.7.) and in all cases the results were expressed as a percentage ratio to the total ion beam for the isotopes measured. The analytical results were compared using Parker's H and C parameters as defined in Appendix 1. Because the precision was 10% replicate determinations were made in most cases, generally four or five replicates being made on each glass.

13.1.1. Discrimination between glasses with the same refractive index and density

Twenty samples were selected within the refractive index range 1.5157-1.5159 and within the density range 2.4824-2.4836. The samples were flat glasses which had been removed from windows in the course of the Fire Survey. Two controls were selected from the twenty by someone acting as referee; the object of the experiment being to correctly link two of the twenty samples, labelled alphabetically A to S in the Tables, to the two controls.

The analytical results for a single analysis on each of the 20 samples and two controls are given in Table 30. The assumed standard deviation given alongside each control was calculated from the coefficients of variation obtained from the previous 20 plates for each isotope. Under these circumstances Parker's Index C can be used to a good approximation (see Appendix 1). It was assumed that there was no correlation between the isotopes.

Two further samples of control 1 were analysed and the means and standard deviations for the three analyses calculated and compared to five of the samples using Parker's H and C indices. The results are given in Table 33.

Further analyses were carried out on samples C, K, Q and T and Parker's H parameter was used to compare these with the control. Table 34 shows the analytical results and Parker's H parameter.

13.1.2. The Variation in Composition between Factories

The variation in composition between different production sites of the same manufacturer was investigated by examining glasses produced at the St. Helens, Queenborough and Pontypool works of Pilkington Brothers. Table 36 shows the analytical results and Table 37 shows the values of Parker's H and C indices when the results in Table 36 are compared.

13.1.3. The Variation in Glass Composition within one factory

The variation of glass composition within one factory was investigated by examining samples from the same factory, but drawn on different days. Table 38 shows the analytical results and the statistical comparison between two glasses produced at the St. Helens Sheet Glass Works of Pilkington Brothers. Table 39 shows the analytical results and the statistical comparison of glass samples taken on two separate dates from the Pontypool works of the same company.

13.1.4. The Difference in Results obtained between two operators

The critical factors affecting the setting up of the electrodes and subsequent sparking were discussed in Section 11.2. Because electrode location is so important the analytical results obtained by two different operators were studied. The same sample of glass was sparked by two different operators and the analytical results are shown in Table 40, together with the statistical comparison.

13.2 DISCUSSION

13.2.1. Discrimination between glasses of the same refractive index and density

An examination of Table 30 shows that the two controls are different from each other; the most marked difference being in the strontium to rubidium ratios. Further examination of the Table shows that control 2 could only be associated with samples B, D, G and J. Table 31 shows Parker's C values for these four samples compared with control 2. C_o at the 1% level is 23.2 and it may be seen that the C values of samples D, G and J greatly exceed this figure. Sample B is much less than C_o and control 2 and sample B are, therefore, classified as similar. This was, in fact, the correct result.

A simple visual comparison between control 1 and the remaining 16 samples shows that many may be eliminated on the basis of the vanadium content alone. Taking the standard deviation into account, control 1 must be either C, E, H, K, M, O, Q, S or T on the basis of a visual inspection of the analytical results. Table 32 shows the values of Parker's C for each isotope for all these samples. Samples E and H may be eliminated because $C > C_o$ and samples S and O are eliminated because the value of C obtained for V-51 is so high. Hence control 1 must come from either C, K, M, Q or T and further samples must be taken for analysis in order to obtain better discrimination. Examination of Table 33 shows that in no case is $H > H_o$ and, therefore, on the basis of the index H all the 5 samples are indistinguishable from control 1. However, for two samples (M and K) $C > C_o$. Table 34 shows that only a slight increase in discrimination has been obtained by making replicate determina-

TABLE 30

20 samples of same refractive index and density. Ratio to total ion beam of isotopes considered.

Sample	A	B	C	D	E	F	G	H	I	J	K	L
Ce-140	.227	-	.270	-	.183	.246	-	-	.244	-	.238	.209
La-139	-	-	-	-	-	-	-	-	-	-	.136	.121
Ba-138	8.13	14.5	8.23	9.03	6.44	8.96	9.39	7.90	8.17	8.06	7.86	8.43
Ba-137	1.23	1.96	1.23	1.31	.887	1.22	1.10	1.05	1.20	.982	1.35	1.20
Zr-90	1.50	1.03	1.74	1.30	1.36	1.23	.769	1.13	1.29	.696	1.65	1.45
Sr-86	.569	3.08	.616	2.89	.560	.534	2.25	.608	.590	2.37	.683	.609
Rb-85	8.03	2.16	7.83	2.28	7.69	8.17	1.90	7.21	6.88	1.98	7.38	8.84
Co-59	.772	.736	.675	.829	.697	.711	.661	.619	.728	.613	.769	.647
Mn-55	27.6	27.2	28.3	30.3	27.6	28.3	27.1	27.7	27.5	28.2	24.2	29.1
Fe-54	9.76	7.03	10.4	9.33	10.8	10.3	7.85	11.7	10.4	7.73	8.77	9.91
V-51	.686	.982	1.20	2.21	.709	.628	2.02	.803	.705	1.78	1.09	.610
Ti-49	2.98	1.09	2.81	2.07	2.88	2.71	1.38	2.60	2.86	1.54	2.99	2.83
Ca-43	38.5	40.0	36.7	38.5	40.2	37.0	45.6	38.5	39.4	46.0	42.9	36.0

TABLE 30 (Continued)

20 samples of same refractive index and density. Ratio to total ion beam of isotopes considered.

Sample	T	Q	M	N	O	P	R	S	Control 1		Control 2	
									Result	S.D.*	Result	S.D.*
Ce-140	.236	.256	.285	.257	.300	.280	.151	.270	.270	.06	0.255	.06
La-139	.133	.157	.163	-	.204	.163	-	.154	.173	.03	.179	.03
Ba.138	8.38	7.88	7.79	6.74	8.14	10.0	1.40	6.73	7.96	1.0	10.7	1.0
Ba-137	1.23	1.27	1.34	1.11	1.48	1.75	.217	1.22	1.27	.2	1.97	.4
Zr-90	1.55	1.46	1.57	1.77	1.43	1.73	1.28	1.54	1.82	.2	1.30	.1
Sr-86	.605	.679	.844	.561	.750	.775	.589	.682	.712	.06	3.52	.3
Rb-85	7.61	7.79	7.63	6.73	7.35	8.22	1.61	6.94	8.01	1.0	2.65	.3
Co-59	.671	.728	.799	.693	.741	.761	.869	.726	.876	.1	1.19	.2
Mn-55	25.8	27.7	27.9	27.8	24.6	22.1	31.7	29.5	27.4	2.0	28.6	2.0
Fe-54	9.65	11.5	12.8	11.6	9.51	9.20	13.9	10.2	10.2	1.0	7.90	1.0
V-51	1.13	1.26	.895	.707	.771	2.15	1.37	.723	1.23	.1	1.13	.1
Ti-49	3.02	2.96	2.99	2.91	3.27	3.07	1.27	3.17	3.27	.2	1.30	.09
Ca-43	39.9	36.4	34.8	39.1	41.4	39.7	45.7	38.1	36.8	3.0	39.4	3.0

* see text

TABLE 31

Control 2 compared with 4 samples using an assumed standard deviation and Parker's C Index

	B	D	G	J
Ba-137	0.	1.36	2.37	3.05
Zr-90	3.65	0.	14.1	18.24
Sr-86	1.08	2.20	8.96	7.35
Rb-85	1.33	.76	3.13	2.49
Co-59	2.58	1.63	3.50	4.16
Mn-55	.24	.36	.28	.02
Fe-54	.38	1.02	0.	.01
V-51	1.10	58.32	39.6	21.12
Ti-49	2.72	36.60	.4	3.56
Ca-43	.02	.04	2.14	2.42
Total C	13.10	102.29	74.48	62.42

$N = 10 \quad C_o\ (1\%) = 23.2$

TABLE 32

Control 1 compared with 9 samples using an assumed standard deviation and Parker's C Index

	C	E	H	K	M	O	Q	S	T
Ce-140	0.	-	-	.14	.03	.12	.03	0.	.16
La-139	-	-	-	.76	.06	.53	.14	.2	.89
Ba-137	.02	1.83	.60	.08	.06	.55	0.	.03	.02
Zr-90	.08	2.64	5.95	.36	.78	1.90	1.62	.98	.91
Sr-86	1.28	3.21	1.50	.12	2.42	.20	.15	.12	1.59
Rb-85	.02	.05	.32	.20	.07	.22	.02	.57	.08
Co-59	2.02	1.60	3.30	.57	.30	.91	1.10	1.13	2.10
Mn-55	.1	0.	.01	1.28	.03	.98	.01	.55	.32
Fe-54	.02	.18	1.13	1.02	3.38	.24	.84	0.	.15
V-51	.04	13.57	9.12	.98	5.61	10.53	.04	12.85	.5
Ti-49	2.64	1.90	2.76	.98	.98	0.	1.20	.12	.78
Ca-43	0.	.64	.16	2.07	.22	1.18	.01	.09	.53
ΣC	6.22	25.62	24.85	8.56	13.94	17.36	5.16	16.64	8.03
N	11	10	10	12	12	12	12	12	12
C_o(1%)	24.7	23.2	23.2	26.2	26.2	26.2	26.2	26.2	26.2

TABLE 33

Mean analytical results obtained from three determinations on control 1 compared to single results obtained for five of the twenty samples using Parker's Comparison Indices

	Analytical Results		Control 1 Compared to Samples Using Parker's Test Statistics									
	Control 1		Sample C		Sample K		Sample M		Sample Q		Sample T	
	Mean	Std. Dev.	H	C	H	C	H	C	H	C	H	C
Ce-140	.269	.031	.00	.00	.64	.75	.19	.2	.13	.13	.71	.85
Ba-138	8.96	.89	-	-	-	-	-	-	-	-	-	-
Ba-137	1.43	.16	.92	1.17	.18	.19	.22	.24	.64	.75	.92	1.17
Zr-90	1.84	.19	.2	.21	.64	.75	1.13	1.51	1.83	3.00	1.26	1.75
Sr-86	.721	.076	1.08	1.43	.18	.19	1.37	1.96	.22	.23	1.26	1.75
Rb-85	8.54	.64	.76	.92	1.61	2.46	1.13	1.52	.83	1.03	1.17	1.58
Co-59	.759	.132	.28	.30	.00	.00	.07	.07	.04	.04	.31	.33
Mn-55	26.3	1.0	1.83	3.00	1.95	3.31	1.35	1.92	1.10	1.47	.18	.19
Fe-54	9.80	.60	.64	.75	1.49	2.21	4.68	18.75	2.78	6.02	.05	.05
V-51	1.24	.03	1.02	1.33	4.68	18.75	7.85	99.19	.31	.33	3.60	10.08
Ti-49	3.13	.22	1.17	1.59	.28	.30	.28	.30	.4	.45	.18	.19
Ca-43	37.0	1.6	.03	.03	3.60	10.07	1.06	1.40	.10	.1	1.59	2.43
Total H or C			7.93	10.74	15.24	38.98	19.32	127.06	8.38	13.55	11.21	20.37
H_o or C_o (1%)			28.7	24.7	28.7	24.7	28.7	24.7	28.7	24.7	28.7	24.7

N = 11 v = 2 in each case

tions on each sample. However, it is now possible to eliminate K because $H > H_o$ at the 5% level, and therefore, on the basis of the above results, control 1 must be associated with samples C, Q or T, with K and M as 'outside chances'.

In Tables 33 and 34 the standard deviations shown were based on relatively few measurements. An alternative approach is to determine the mean values from the replicate determinations for each isotope as given in Tables 33 and 34, but to use the assumed standard deviations from 20 earlier plates, as previously discussed. Table 35 shows the values of C obtained using this procedure. In Tables 34 and 35 the total values of Parker's C and H criteria shown for samples T and C are both very low and, therefore, control 1 is most likely to be associated with one of these.

Therefore, taking all the results into consideration, samples T and C, and possibly sample Q, are most likely to have originated from control 1 with samples K and M as 'outside chances'. The correct answer is that sample T came from control 1.

13.2.2. Variation in Composition between factories

Tables 36 and 37 show that by using the statistical technique described by Parker it is possible to distinguish between glasses produced at three different factories. The glass from both Queenborough and Pontypool has a composition markedly different from the St. Helens glass; the main difference being that in the case of St. Helens glass, the rubidium to strontium ratio is about 10 whilst in the case of Queenborough and Pontypool glass the ratio is about 1. This differ-

TABLE 34

Mean result from Control 1 compared to mean results obtained from replicate determinations made on four of the twenty samples using Parker's H Index.

Sample	C			K			Q			T		
No. of replicates	5			4			3			4		
	Mean	Std. Dev.	H	Mean	Std. Dev.	H	Mean	Std. Dev.	H	Mean	Std. Dev.	H
Ce-140	.294	.022	.89	.250	.012	1.17	.318	.054	1.53	.275	.062	.02
Ba-138	9.46	1.73	-	7.74	.79	-	7.91	1.88	-	8.87	1.59	-
Ba-137	1.46	.22	.58	1.24	.14	2.23	1.47	.29	.04	1.32	.17	.70
Zr-90	1.76	.10	.29	1.57	.09	4.15	1.49	.04	4.94	1.62	.15	2.33
Sr-86	.689	.059	.13	.637	.048	2.52	.724	.044	0.00	.643	.075	1.56
Rb-85	7.53	.29	1.81	8.03	.80	.75	7.22	.50	4.37	7.99	.89	.75
Co-59	.789	.120	.42	.635	.096	1.76	.787	.096	.09	.655	.074	1.54
Mn-55	26.8	2.8	.03	28.6	3.0	1.36	27.9	1.9	1.39	26.5	1.0	.07
Fe-54	10.3	1.2	.01	10.4	1.2	.58	11.3	.8	3.95	9.82	.19	0.00
V-51	1.22	.10	.01	1.12	.06	5.42	1.32	.08	2.02	1.18	.03	4.32
Ti-49	2.75	.16	4.65	2.89	.15	2.35	3.18	.27	.06	3.00	.05	1.23
Ca-43	36.8	2.0	0.0	36.8	4.1	.01	36.4	.8	.32	38.2	2.2	.59
Total H			8.82			22.30			18.71			13.11
V			6			5			4			5
H_o (1%)			25.8			26.2			26.8			26.2
H_o (5%)			20.6			20.8			21.1			20.8

In all cases N = 11

TABLE 35

The mean of Control 1 compared with the means of 4 samples using an assumed standard deviation and Parker's C Index

		Control	C		K		Q		T	
No. of Determinations		3	5		4		3		4	
	Std. Dev.	Mean	Mean	C	Mean	C	Mean	C	Mean	C
Ce-140	.06	.269	.294	.33	.250	.17	.318	1.0	.275	.02
La-139	.03	-	-	-	-	-	-	-	-	-
Ba-137	.2	1.43	1.46	.04	1.24	1.55	1.47	.06	1.32	.52
Zr-90	.2	1.84	1.76	.30	1.57	3.12	1.49	4.59	1.62	2.07
Sr-86	.06	.721	.689	.53	.637	3.36	.724	.00	.643	2.90
Rb-85	1.0	8.54	7.53	1.91	8.03	.45	7.22	2.61	7.99	.52
Co-59	.1	.759	.789	.17	.635	2.64	.787	.12	.655	1.85
Mn-55	2.0	26.3	26.9	.17	28.6	2.27	27.9	.96	25.5	.02
Fe-54	1.0	9.80	10.3	.47	10.4	.62	11.3	3.38	9.82	.00
V-51	.1	1.24	1.22	.08	1.12	2.47	1.32	.96	1.18	.62
Ti-49	.2	3.13	2.75	6.77	2.89	2.47	3.18	.09	3.00	.72
Ca-43	3.0	37.0	36.8	.01	36.8	.01	36.4	.06	38.2	.27
ΣC				10.77		19.11		13.84		9.51
C_o (5%)				19.68		19.68		19.68		19.68

N = 11

TABLE 36

Analytical results and precision obtained on glass taken from three different factories on known dates

No. of determinations	4			4			5		
Factory	St. Helens 17/7/67			Queenborough 19/7/67			Pontypool 19/7/67		
	Mean	Std. Dev.	C. of V. %	Mean	Std. Dev.	C. of V. %	Mean	Std. Dev.	C. of V. %
Ce-140	.515	.062	12.1	.337	.026	7.8	.305	.053	17.2
La-139	.303	.033	10.8	.212	.023	10.6	.201	.022	11.0
Ba-138	10.7	2.7	25.3	15.8	2.35	14.9	12.5	1.06	8.5
Ba-137	1.95	.49	25.0	2.82	.265	9.4	2.04	.291	14.3
Zr-90	2.66	.19	7.2	1.80	.049	2.7	1.32	.088	6.7
Sr-86	.964	.126	13.1	4.66	.504	10.8	4.09	.37	9.2
Rb-85	9.42	1.35	14.3	4.34	.40	9.3	3.62	.51	14.1
As-75	.264	.049	18.4	.449	.133	29.7	.334	.068	20.3
Co-59	.824	.162	19.7	.844	.167	19.7	1.33	.24	18.3
Mn-55	27.6	4.0	14.5	26.8	2.0	7.6	27.3	1.4	5.3
Fe-54	11.4	2.1	18.3	8.37	1.50	18.0	8.73	.56	6.4
V-51	2.76	.24	8.6	1.91	.18	9.6	2.04	.27	13.3
Ti-49	3.73	.22	5.8	1.85	.17	9.2	1.87	.16	8.5
Ca-43	27.2	2.6	9.5	29.8	2.20	7.4	35.5	1.4	4.0
Mean C. of V. %			14.5			11.9			11.2

TABLE 37

The Comparison of the three pairs of glasses in Table 27 using Parker's H and C indices

	St. Helens and Q'Boro		St. Helens and Pontypool		Q'Boro and Pontypool	
	H	C	H	C	H	C
Ce-140	10.4	37.5	11.7	13.1	1.1	.3
La-139	8.9	12.5	11.9	17.9	.5	.2
Ba-137	5.8	8.7	.1	.1	8.7	6.0
Zr-90	15.8	247.6	23.7	193.2	18.6	24.6
Sr-86	21.3	43.0	25.4	187.5	3.1	2.0
Rb-85	13.6	129.0	17.7	107.8	3.9	1.7
As-75	4.6	1.5	2.5	.9	2.4	2.4
Co-59	.03	.01	7.3	3.7	6.9	3.4
Mn-55	.01	.01	.03	.04	.2	.1
Fe-54	3.9	3.3	5.2	18.9	.2	.3
V-51	11.1	17.8	8.7	5.9	.6	.2
Ti-49	20.7	97.8	24.3	112.6	.03	.01
Ca-43	1.9	1.1	11.6	22.7	8.2	9.6
Σ H	118.2	-	150.0	-	54.7	
Σ C	-	600.0	-	684.4	-	50.7
ν†	6	-	7	-	7	-
N*	14	-	14	-	14	-
H_o(1%)	30.7	-	30.4	-	30.4	-
C_o(1%)	-	29.1	-	29.1	-	29.1
	Queenborough is control		Pontypool is control		Pontypool is control	

† number of degrees of freedom (see Appendix 1)

* number of characteristics (" " ")

ence in relative abundances may be due to differences in the ages of the sand from which the glasses were made. It is interesting to note that Table 37 shows that in 2 out of the 3 comparisons made, the C parameter gives a much higher total. This is the effect of assuming that the standard deviation is accurately known. With H the standard deviation is estimated from the available data and hence there is an uncertainty in the standard deviation. This uncertainty is reflected in the lower numerical value of H.

13.2.3. The Variation in glass composition within one factory

The results in Tables 38 and 39 show that the two samples from St. Helens could not be distinguished from each other, but that the two from Pontypool could. It would require a prolonged study to collect enough analytical information about modern window glass in order to be able to evaluate the discriminating power of the technique for this type of glass. Moreover, the samples used had not been exposed to any weathering process. Electron microscopy[214] has shown that weathering has an effect on the surface of glass and it is possible that weathering will produce an alteration in the elemental concentrations in the glass.

13.2.4. The Difference in Results obtained between two operators

If a method is to become a useful technique in Forensic science, it is important that operator error is small so that survey results obtained by one individual may be used by another without introducing unacceptable errors. Table 40 illustrates that the results obtained by two different operators are not sig-

TABLE 38

Analytical results and Parker's Comparison Indices for two glasses manufactured at St. Helens Sheet Glass Works.

Date of Manufacture	17/7/67			4/1/68				
No. of replicates	4			4				
	Mean	Std. Dev.	C. of V. %	Mean	Std. Dev.	C. of V. %	H.	C
Ce-140	.567	.078	14	.517	.068	13	.87	.33
La-139	.335	.041	12	.297	.017	6	2.39	.69
Ba-138	11.8	3.13	26	12.5	1.7	14	-	-
Ba-137	2.15	.57	26	2.20	.28	13	.02	.01
Zr-90	2.93	.22	8	2.67	.27	10	1.90	1.12
Sr-86	1.06	.152	14	1.00	.09	9	.44	.12
As-75	.292	.054	18	.309	.057	18	.18	.08
Co-59	.913	.193	21	1.30	.39	30	2.54	3.22
Mn-55	30.4	4.1	14	30.25	3.9	13	.00	.00
Fe-54	12.6	2.1	17	11.8	.88	8	.47	.12
V-51	3.04	.21	7	2.58	.19	7	6.09	3.84
Ti-49	4.13	.20	5	3.64	.21	6	6.40	4.80
Ca-43	30.0	3.0	10	31.0	3.8	12	.17	.09
Total H or C							21.48	14.41
H_o(1%) or C_o(1%)							27.4	26.2

v = 6 N = 12.

TABLE 39

Analytical results and Parker's Comparison Indices

for two glasses manufactured at Pontypool.

Date of Manufacture	30/7/67			30/8/67				
No. of replicates	4			4				
	Mean	Std. Dev.	C. of V. %	Mean	Std. Dev.	C. of V. %	H	C
Ce-140	.211	.072	33.9	.218	.054	24.8	.02	.01
La-139	-	-	-	.144	.035	24.0	-	-
Ba-137	1.47	.25	17.2	1.96	.32	16.5	4.07	3.07
Zr-90	1.24	.14	11.1	1.19	.15	12.9	.23	.10
Sr-86	3.17	.12	3.80	3.50	.31	8.8	3.03	6.05
Rb-85	2.64	.27	10.3	3.34	.36	10.6	5.76	5.38
As-75	.377	.080	21.1	.279	.045	16.0	3.39	1.20
Co-59	1.15	.14	12.0	.917	.083	9.1	5.17	2.22
Mn-55	28.7	.99	3.44	28.9	3.1	10.6	.02	.03
Fe-54	11.5	1.8	15.8	9.65	1.39	14.4	2.19	.85
V-51	2.57	.29	11.4	2.23	.13	5.7	3.40	1.10
Ti-49	1.81	.13	7.4	1.56	.09	5.7	5.88	2.96
Ca-43	37.0	3.63	9.8	34.2	3.1	9.0	1.24	.48
Total H or C							34.41	23.44
H_o (1%) or C_o (1%)							27.4	26.2

v = 6 N = 12

TABLE 40

Analytical results and comparison of the same sample of glass (Pontypool 19/7/67) sparked by two different operators.

	1st operator (5 determinations)			2nd operator (3 determinations)			
	Mean	Std. Dev.	C. of V. %	Mean	Std. Dev.	C. of V. %	H
Ce-140	.305	.053	17.2	.293	.044	14.8	.11
La-139	.201	.022	11.0	.188	.026	13.7	.55
Ba-137	2.04	.291	14.3	2.40	.19	7.7	2.79
Zr-90	1.32	.088	6.7	1.40	.10	7.1	1.27
Sr-86	4.09	.37	9.2	4.06	.09	2.1	.02
Rb-85	3.62	.51	14.1	4.10	.09	2.2	2.06
As-75	.334	.068	20.3	.397	.037	9.4	1.80
Co-59	1.33	.24	18.3	1.38	.24	17.4	.08
Mn-55	27.3	1.4	5.3	28.0	2.8	9.9	.23
Fe-54	8.73	.56	6.4	9.64	.57	5.9	3.58
V-51	2.04	.27	13.3	2.13	.24	11.4	.22
Ti-49	1.87	.16	8.5	2.04	.087	4.3	3.06
Ca-43	34.5	1.4	4.0	31.3	2.1	6.6	4.60
$\sum H$							20.36
$H_o(5\%)$							23.6

N = 13 v = 6

nificantly different from each other because H is less than H_o even at the 5% level.

.14. CONCLUSIONS

The work described in this thesis has shown that density and refractive index are useful parameters for the comparison of glass fragments. Techniques using refractive index have the advantage over techniques using density in that the former are uneffected by traces of dirt, grease, cracks, etc. on the surface of the glass. The Mettler hot-stage enables measurements of refractive index to be made with a standard deviation of only 0.00002 on very small samples (< 1mg) and because it is already possible to detect the variation across a pane of glass using this method, it is not necessary to seek a more sensitive technique at the present time.

The sink/float method for the determination of density which was found to be satisfactory for this study, is time consuming and yields a precision of 0.0004g cm^{-3}. Linear density gradients offer an alternative method for the determination of the density of small fragments of glass and preliminary experiments are being carried out. For large pieces of glass (15g or over) Archimedes method was shown to be satisfactory giving a precision of 0.0003g cm^{-3}.

The difficulties involved in the selection of a suitable population from which to predict the frequency of occurrence of glass samples has been emphasized, but there is a clear case for using the results from the survey of samples of glass removed from the scenes of fires by Fire Officers. It is obvious from the survey of glass on clothing that glasses other than flat window glass are found on clothing. Therefore, the properties of other types of glass used to make containers, vehicle headlamps, windscreens, etc. will have to be investigated before the com-

plete pattern of the properties of broken glass in the country can be built up. Under these circumstances, the development of a simple reliable technique to distinguish between the different types of glass would be very useful and would enable a precise statistical treatment to be applied to any future survey of such glasses.

The statistical treatment of refractive index and density described in Section 8 provides a statistical assessment of the analytical results obtained in a Forensic Science laboratory and compares them with the properties of a known population of glasses. It is emphasized that the treatment only considers the analytical results and does not take into account the particular circumstances which may surround a given case. For example, the suspect may be a glazier or be otherwise employed where he may be in contact with considerable amounts of broken glass. It is the forensic scientist's job to take into account any circumstances surrounding a given case before presenting evidence in court. It is a fact that people employed in certain occupations are more likely to get certain types of glass on their clothing and, therefore, in these circumstances the probabilities provided by the Fire Survey alone may well lead to misleading conclusions.

As the proportion of modern window glass in the country increases the value of refractive index and density as discriminatory techniques will diminish and it will be necessary to find additional parameters for comparison. Mass spectrometry (or any similar method of trace element analysis) has been shown to be useful in the analysis of glass. The average coefficient of variation for 10 elements was found to be approximately 10% and

this enabled glasses produced in different factories with the same nominal composition to be distinguished. However, at the present time it is not possible to distinguish reliably between glasses produced at the same factory, using raw materials taken from the same source, and producing glass with the same nominal composition. Increasing the precision will increase discrimination sharply and it can be seen from Appendix 1 that the discrimination will increase as the square of the increase in precision. Therefore, there are excellent reasons why every effort should be made to increase precision.

A number of procedures for the evaluation of mass spectrometry photoplates have been investigated. The Wagner method provides a simple yet precise technique for the quantitative evaluation of mass spectrometric data and is capable of yielding a precision of better than 10%. It has the advantage over the simple graphical method in that the slope is fixed, but suffers from the disadvantage that the point at which the curve deviates from linearity varies from plate to plate. This latter factor precluded its use in this study.

The linearized Hull equation provides an excellent method for the interpretation of photoplates and computer programmes have been developed which enable the necessary calculations to be carried out on a small desk computer. The Hull equation has enabled a completely objective approach to be made to the interpretation of photoplates and has removed almost all the subjectivity inherent in graphical methods. Therefore, the use of this equation is recommended when dealing with mass spectrometric data in Forensic Science.

When this study was initiated the value of modern glass as evidence was intuitive rather than objective. The result of this study has been to improve considerably the objectivity. It has been pointed out by Pearson(218) that the probability of finding a sample of glass on clothing with a given analysis in the modern range can be as low as 1 in 1500, the total probability being built up as follows:-

Chance of finding a glass fragment as large as 1mg on clothing	∽ 1 in 10
Chance of glass on clothing being window glass	∽ 1 in 3
Chance of glass being in modern range	∽ 1 in 5
Increase in discrimination using mass spectrometry	∽ 1 in 10

Therefore, it is clear that if all available methods are used, glass can provide exceedingly good evidence.

APPENDIX. 1

The Comparison of Glasses using Parker's Method

In the sections dealing with the physical properties of glasses it was necessary to have some sort of statistical test for the comparison of two glasses. In the examination of the physical properties only one or two parameters are being dealt with, but in the case of mass spectrometry, the relative concentrations of perhaps 10 or 20 elements are determined. Clearly to make full use of this data it is necessary to use a sound statistical approach so the decision as to whether two samples are similar or not is arrived at quantitatively and not by inspired guesswork.

Parker has written a series of three excellent papers [60,61,92] concerned with the problem of comparing the characteristics of samples with particular reference to the problems of Forensic Science. Because the subject is so important in the comparison of modern window glass, the method will be described here from this viewpoint.

In this study we are only concerned with characteristics which can have a numerical value assigned to them, e.g. the concentration of an element. The technique is unsuitable for the examination of discrete data such as the colour of an object, fingerprints, shoe prints, etc.

When any chemical analysis is performed there is an error associated with the measurement. The smaller this error the more precise is the measurement. In addition to the experimental error, there may be variation within the sample itself so that even if the experimental error is zero, this intrinsic variation will lead to different results being obtained in a

series of replicate analyses. This intrinsic variation is common, for example, in the analysis of human hair and in the analysis of certain mineral ores. Finally there are the differences that will occur between members of the same population, i.e. the differences between hairs from different people or ore from different mines. It is clear, therefore, that in order to distinguish between members of the same population whose characteristics only differ by small amounts, it is necessary for the experimental error to be as small as possible. Also the intrinsic variation should be small. If the intrinsic variation becomes approximately the same as the variation in the population, then it will be impossible to distinguish between any samples from that population.

The general approach is to define a 'discrepancy index' C which is defined as the sum of the squares of the standardized differences between the same characteristic for the two objects. The objects may be samples of glass from two different factories or they may consist of one sample of glass removed from a person's clothing (the sample) and a number of fragments of glass removed from the scene of the crime (the control). The samples could equally well be hairs, fibres or paint or anything else which could be analysed and a numerical value of a characteristic obtained. C is compared to a threshold index C_o which is dependent on the number of characteristics measured. C_o is chosen so that the chance of a characteristic having a value of $C > C_o$ when they do in fact come from the same source is some given quantity ϵ. If ϵ is chosen to be very small, the chance that $C > C_o$ will be correspondingly small and, therefore, it is unlikely that two

samples from the same source will appear different. However, if ϵ is too small, many other people or objects quite unconnected with each other will have a C value less than C_o for a given characteristic and the test will be too insensitive. A commonly accepted value for ϵ is .01 which means that only once in every 100 trials will $C > C_o$ when the two samples do, in fact, have a common origin.

Let it be assumed that there are N characteristics available for numerical comparison. Generally there are a number of controls available from the scene of the crime and each is measured individually and the results averaged. Therefore, the following can be defined:-

X = the value of the characteristic obtained for the sample or the mean of n_1 observations.

Y = the value of the characteristic obtained for the control or the mean value of n_2 observations.

ϕ = standard deviations of the means of sets of n_2 readings taken on the controls.

θ = standard deviations of the means of sets of n_1 readings taken on the sample.

σ = standard deviation of individual measurements taken on an infinite number of single samples.

θ, ϕ and σ include errors of measurement, errors in analysis and errors due to the intrinsic or natural variation which may occur over the domain from which the sample was taken. In many cases σ will not be known and will have to be estimated. Alternatively, a reasonable number of controls may be taken (10 for example) and the standard deviation calculated and this value

assumed to be the true population standard deviation σ. Under certain conditions this approach has been used by Parker[61]. The results from all determinations should be normally distributed around the mean value.

If both sample and control do in fact have common origin, the expectation of X - Y is zero with standard deviation λ. λ is calculated from the law of errors and is defined as

$$\lambda = \sqrt{\phi^2 + \theta^2} \quad \text{---------- (1)}$$

The 'discrepancy index' C can now be defined as

$$C = \sum_{1}^{N} D^2 \quad \text{---------- (2)}$$

where D is the reduced difference with unit standard deviation and is given by

$$D = \frac{X - Y}{\lambda} \quad \text{---------- (3)}$$

If the N characteristics are uncorrelated and both ϕ and θ are accurately known, C is the sum of squares of N random normal deviates each with unit standard deviation. If the crime and control samples do, in fact, come from the same source, the expectation of all the values of D is zero. To determine if the sample and control are similar, the value of C obtained is compared with a threshold value of C_o which is obtained from suitable percentage points of the χ^2 distribution with N degrees of freedom. If $C < C_o$ the two samples are similar.

As pointed out above, in some cases σ is not known, but it may be assumed that σ is equal to the standard deviation of the n_2 controls providing that n_2 is large enough (10 or more).

In the common case where there are n_2 controls and a single sample this means that X is measured with a standard deviation of σ and Y is measured with a standard deviation which is given by the equation

$$\phi = \frac{\sigma}{\sqrt{n_2}} \quad \text{----------} \quad (4)$$

Hence from equation 1

$$\lambda = \sqrt{\sigma^2 + \frac{\sigma^2}{n_2}}$$

$$= \sqrt{\sigma^2\left(1 + \frac{1}{n_2}\right)}$$

$$\therefore \quad \lambda = \sigma\sqrt{1 + \frac{1}{n_2}} \quad \text{----------} \quad (5)$$

It is interesting to note from equation 4 that as n_2 increases ϕ decreases. Similarly, θ decreases as n_1 increases, and this is the mathematical justification for making replicate determinations.

It is worthy of note at this point that the standard deviation calculated from the n_2 determinations should include Bessel's[96] correction, i.e.

$$\sigma^2 = \frac{\sum (x - \bar{x})^2}{n - 1} \quad \text{----------} \quad (6)$$

If there is no information available to establish the value of ϕ and θ because perhaps, there are a limited number of controls or there are several samples, then ϕ and θ must be estimated from the $n_1 + n_2$ determinations themselves. Let U be the variance of n_1 observations made on the sample and V be the

variance of n_2 observations made on the control. Also let the variance of $(X - Y)$ be defined as L^2 (where L^2 is the variance based on $n_1 + n_2$ measurements, c.f. λ^2).

U and V are two 'best estimates' of the total population variance σ^2 and have been calculated using equation 6. To calculate the 'best estimate' of the population variance based on $n_1 + n_2$ observations, it is necessary to apply Bessel's correction in reverse and calculate the actual sample variances s_1^2 and s_2^2 for the n_1 and n_2 readings respectively. For example for U

$$U = \left(\frac{n_1}{n_1 - 1}\right) s_1^2$$

$$\therefore \quad s_1^2 = U\left(\frac{n_1 - 1}{n_1}\right) \quad \text{- - - - - - - - - - -} \quad (7)$$

and similarly for V and s_2^2.

Having obtained s_1 and s_2, the best estimate of the population variance may be calculated taking n_1 and n_2 into account. (It would obviously be wrong to place as much reliance on a standard deviation calculated from a sample of 5 readings as from a sample of 100 readings).

Again using Bessel's correction we have

$$\hat{\sigma}^2 = s_1^2\left(\frac{n_1}{n_1 - 1}\right)$$

$$\therefore \quad s_1^2 n_1 = \hat{\sigma}^2(n_1 - 1) \quad \text{- - - - - - - - - - -} \quad (8)$$

where $\hat{\sigma}^2$ = best estimate of population variance.

and similarly

$$\hat{\sigma}^2 = s_2^2\left(\frac{n_2}{n_2 - 1}\right)$$

$$\therefore\ s_2^2 n_2 = \hat{\sigma}^2\,(n_2 - 1) \text{ - - - - - - - - - - - - (9)}$$

From 8 and 9

$s_1^2 n_1$ is an estimate of $\hat{\sigma}^2(n_1 - 1)$

$s_2^2 n_2$ " " " " $\hat{\sigma}^2(n_2 - 1)$

Adding $s_1^2 n_1 + s_2^2 n_2$ " " " " $\hat{\sigma}^2(n_1 + n_2 - 2)$

$$\therefore\ \hat{\sigma}^2 = \frac{s_1^2 n_1 + s_2^2 n_2}{n_1 + n_2 - 2} \text{ - - - - - - - - - - - (10)}$$

The standard deviation of the mean value of the control is given by $\frac{\sigma}{\sqrt{n_2}}$. Similarly the standard deviation of the mean value of the sample is given by $\frac{\sigma}{\sqrt{n_1}}$

Therefore, the variance of X - Y is given by

$$L^2 = \frac{\sigma^2}{n_1} + \frac{\sigma^2}{n_2}$$

$$= \sigma^2\left(\frac{1}{n_1} + \frac{1}{n_2}\right) \text{ - - - - - - - - - - (11)}$$

Putting $\sigma = \hat{\sigma}$ and substituting equation 10 into equation 11 gives

$$L^2 = \frac{s_1^2 n_1 + s_2^2 n_2}{n_1 + n_2 - 2}\left(\frac{1}{n_1} + \frac{1}{n_2}\right) \text{ - - - - - (12)}$$

But from equation 7 it may be seen that

$$s_1^2 n_1 = U(n_1 - 1)$$

and similarly for s_2^2 and V. Substituting this information into equation 12 gives

$$L^2 = \frac{U(n_1 - 1) + V(n_2 - 1)}{n_1 + n_2 - 2} \left(\frac{1}{n_1} + \frac{1}{n_2}\right) \quad - - (13)$$

Equations 12 and 13 give the same answers except in the important case when n_1 or n_2 is equal to 1. In this case, whichever value of n is equal to 1, causes $U(n_1 - 1)$ or $V(n_2 - 1)$ to become zero, thereby removing it from consideration in the estimation of L^2 (c.f. standard deviation with and without Bessel's correction).

An index could then be defined as

$$C' = \sum_1^N \left[\frac{(X - Y)^2}{L^2}\right]$$

but this is no longer distributed as χ^2 and is, in fact, distributed as N t^2 distributions, each with $(n_1 + n_2 - 2)$ degrees of freedom.

Parker has discussed several possible solutions to this problem, but concludes that the best way is to define a test statistic H where

$$H = \sum_1^N v \ln\left(1 + \frac{D^2}{v}\right)$$

where v = number of degrees of freedom = $n_1 + n_2 - 2$

and $D = \frac{X - Y}{L}$

However, H is not distributed in a manner similar to any of the well known distributions and, therefore, its upper percentage points (H_o) must be calculated. Parker and Holford[92] have carried out these calculations and have constructed tables

showing the values of H_o at the 5% and 1% levels for various values of N and n.

Generally the two parameters described (H and C) have been found to be very useful in the comparison of a series of analytical results. However, the interpretation becomes more difficult in a situation where most of the characteristics of two samples agree, but there is one characteristic which gives a very high value of C (or H). Consider the situation where there are 2 samples for comparison and the analytical results are obtained for 10 characteristics. In addition, it is assumed that for 9 of these characteristics the average difference between the two samples is only 0.7 standard deviations and, therefore, the total C value for the 9 characteristics is 4.41. C_o for 10 characteristics is 23.2 and, therefore, the 10th characteristic in the 2 samples under consideration could be as much as 4.2 standard deviations apart, yet the two samples would still be classified as similar. Clearly it is unlikely that these two samples are similar due to the wide discrepancy of the 10th characteristic. Parker does not suggest any way of overcoming this problem, but experience of the method has shown that any single value of C above 6.6 (the value of C_o for 1 characteristic) should be treated with suspicion and the samples classified as different. Alternatively, further analytical measurements may be made.

APPENDIX. 2

Parker's Approach for Correlated Variables

Parker has described a statistical technique for the comparison of the characteristics of two samples and this is set out in detail in Appendix 1. For uncorrelated variables he has defined a discrepancy index C where

$$C = \sum_{1}^{N} \left(\frac{X - Y}{\sqrt{\theta^2 + \phi^2}} \right)^2 \quad \text{---------(1)}$$

where X = is the value obtained for the sample.

Y = the mean value of n_2 measurements made on the control.

θ = the standard deviation of the sample.

ϕ = the standard deviation of a number of sets of n_2 measurements on the control.

If X and Y do in fact come from the same source, the expectation of X - Y is zero and if the N characteristics are uncorrelated C is the sum of N random normal deviates each with unit standard deviation. C will, therefore, be distributed as χ^2 with N degrees of freedom.

In the case of correlated variables where the correlation coefficients are known, it is necessary to define a new index C" and using matrix notation Parker showed that

$$C'' = D^T W^{-1} D \quad \text{----------(2)}$$

where $D = \dfrac{X - Y}{\sqrt{\theta^2 + \phi^2}}$

W = the dispersion matrix or correlation matrix.

Glennie[97] has shown that this equation can be transformed to conventional algebra for two characteristics.

$$C'' = D^T W^{-1} D$$

$$= \frac{1}{1-\rho^2}\left(D_1^2 - 2\rho D_1 D_2 + D_2^2\right)$$

$$= \frac{1}{1-\rho^2}\left[\left(\frac{X_1 - Y_1}{\lambda_1}\right)^2 - \frac{2\rho(X_1 - Y_1)(X_2 - Y_2)}{\lambda_1 \lambda_2} + \left(\frac{X_2 - Y_2}{\lambda_2}\right)^2\right] \quad (3)$$

where X and Y are defined as above and the subscripts 1 and 2 refer to characteristics 1 and 2. λ is equal to $\sqrt{\theta^2 + \phi^2}$ and ρ is the correlation coefficient.

C" is then distributed as χ^2 and the values of C''_o will be the same as C_o at the respective percentage points. Hence both refractive index and density may be taken into account if the correlation between them is known. In the case where the correlation is unknown and must be estimated from the available data, C" is no longer distributed as χ^2 with N degrees of freedom, but is a multiple of Hotelling's T^2. This is distributed as a multiple $\frac{N(n_1 + n_2 - 2)}{n_1 + n_2 - N - 1}$ of the F distribution with degrees of freedom N and $n_1 + n_2 - N - 1$. However, in this case, the limits become so wide that very large differences must occur before samples become statistically different. Therefore, in the case of the correlation being unknown, the test is not very useful.

The estimation of correlation coefficients presents some problems to which there is no easy solution. For example, should the correlation coefficient between two characteristics in samples taken from a single source be studied (e.g. across a

single head of hair or across a single pane of glass,) or the correlation between two characteristics in samples taken from the whole population? The problem is complex and has been discussed elsewhere[99]. The approach to the problem will depend on how the various characteristics vary in the material under examination. In the case of glass fragments, the variation in refractive index and density over the control will be small; in fact, only slightly larger than the error in the method itself. Therefore, it would be difficult to accurately measure the correlation coefficient over a single pane of glass[99] and in this particular case it is better, although theoretically incorrect, to use the correlation coefficient determined from over the whole population.

Equation 3 has some rather interesting properties and should be used with a certain degree of caution. The equation compares the discrepancies between the sample and the control glass for both characteristics and in addition it takes into account the correlation between the discrepancies. In certain closely defined cases this can have the effect of reducing C" so that samples which appear to be different when only one parameter is considered are, in fact, classified as similar when two parameters are compared[99].

APPENDIX. 3

Computer Programme, for Hewlett-Packard 9100B, to calculate the slope parameter v in the Equation of Franzen and Schuy.

The following programme is written using Hewlett-Packard mnemonics.

Instructions

Index Go to - 0 0

" N (number of data points 4-8 inc.)

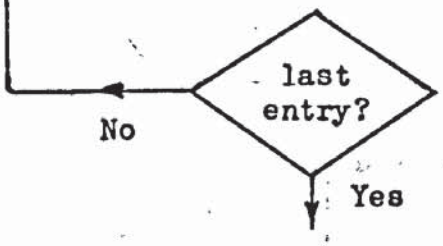
" Cont.

" H_s

" Cont.

" E in z
" H_b " y
" H_{bl} " x

" Cont.



Index Go to - 0 0

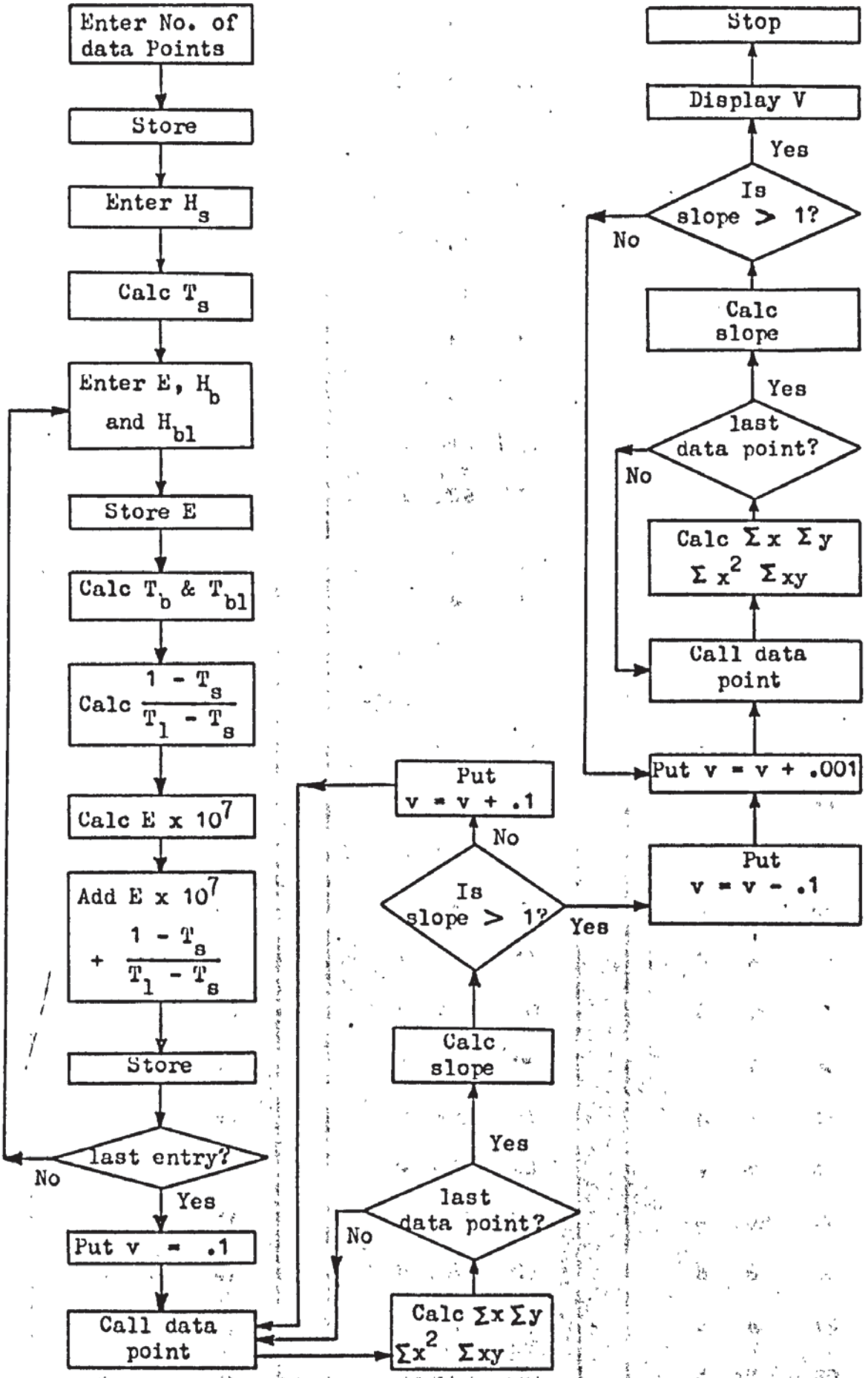
Insert 2nd side and press 'enter'

Index Go to - 0 0

" Cont.

Display v - - - x

Flow Chart for calculation of v.



1st Side

Step	Key	Code
-0-0	XTO	23
1	-	34
2	f	15
3	1	01
4	.	21
5	XTO	23
6	a	13
7	CLR	20
8	XTO	23
9	d	17
a	XTO	23
b	C	16
c	XTO	23
d	b	14
-1-0	STP	41
1	GTO	44
2	SUB	77
3	a	13
4	7	07
5	XTO	23
6	-	34
7	e	12
8	STP	41
9	CNT	47
a	CNT	47
b	CNT	47
c	CNT	47
d	CNT	47

Step	Key	Code
-2-0	CNT	47
1	CNT	47
2	CNT	47
3	CNT	47
4	CNT	47
5	CNT	47
6	CNT	47
7	CNT	47
8	CNT	47
9	GTO	44
a	SUB	77
b	6	06
c	a	13
d	YTO	40
-3-0	7	07
1	STP	41
2	GTO	44
3	SUB	77
4	6	06
5	a	13
6	YTO	40
7	6	06
8	STP	41
9	GTO	44
a	SUB	77
b	6	06
c	a	13
d	YTO	40

Step	Key	Code
-4-0	5	05
1	STP	41
2	GTO	44
3	SUB	77
4	6	06
5	a	13
6	YTO	40
7	4	04
8	STP	41
9	GTO	44
a	SUB	77
b	6	06
c	a	13
d	YTO	40
-5-0	3	03
1	STP	41
2	GTO	44
3	SUB	77
4	6	06
5	a	13
6	YTO	40
7	2	02
8	STP	41
9	GTO	44
a	SUB	77
b	6	06
c	a	13
d	YTO	40

Step	Key	Code
-6-0	1	01
1	STP	41
2	GTO	44
3	SUB	77
4	6	06
5	a	13
6	YTO	40
7	0	00
8	STP	41
9		
a	RUP	22
b	XTO	23
c	-	34
d	d	17
-7-0	DN	25
1	GTO	44
2	SUB	77
3	a	13
4	7	07
5	XEY	30
6	GTO	44
7	SUB	77
8	a	13
9	7	07
a	UP	27
b	RDN	31
c	XEY	30
d	-	34

Step	Key	Code
-8-0	XFR	67
1	-	34
2	e	12
3	RUP	22
4	XEY	30
5	-	34
6	RDN	31
7	DIV	35
8	1	01
9	RUP	22
a	-	34
b	RDN	31
e	x	36
d	1	01
-9-0	XEY	30
1	-	34
2	1	01
3	RUP	22
4	-	34
5	RUP	22
6	XEY	30
7	-	34
8	DN	25
9	DIV	35
a	XFR	67
b	-	34
c	d	17
d	UP	27

Step	Key	Code
-a-0	EEX	26
1	7	07
2	x	36
3	DN	25
4	+	33
5	RTN	77
6		
7	UP	27
8	1	01
9	2	02
a	1	01
b	DIV	35
c	1	01
d	EXP	74
-b-0	LOG	75
1	DIV	35
2	DN	25
3	EXP	74
4	UP	27
5	1	01
6	XEY	30
7	DIV	35
8	DN	25
9	RTN	77
a	END	46
b		
c		
d		

2nd side

Step	Key	Code
-0-0	a	13
1	UP	27
2	.	21
3	1	01
4	+	33
5	YTO	40
6	a	13
7	GTO	44
8	SUB	77
9	3	03
a	c	16
b	CLR	20
c	XTO	23
d	d	17
-1-0	XTO	23
1	c	16
2	YE	24
3	b	14
4	1	1
5	X<Y	52
6	0	00
7	0	00
8	a	13
9	UP	27
a	.	21
b	1	01
c	-	34
d	YTO	40

Step	Key	Code
-2-0	a	13
1	a	13
2	UP	27
3	EEX	26
4	3	03
5	CHS	32
6	+	33
7	YTO	40
8	a	13
9	GTO	44
a	SUB	77
b	3	03
c	c	16
d	CLR	20
-3-0	XTO	23
1	d	17
2	XTO	23
3	c	16
4	YE	24
5	b	14
6	1	01
7	X<Y	52
8	2	02
9	1	01
a	a	13
b	STP	41
c	XFR	67
d	7	07

Step	Key	Code
-4-0	GTO	44
1	SUB	77
2	9	11
3	a	13
4	XFR	67
5	6	06
6	GTO	44
7	SUB	77
8	9	11
9	a	13
a	XFR	67
b	5	05
c	GTO	44
d	SUB	77
-5-0	9	11
1	a	13
2	XFR	67
3	4	04
4	GTO	44
5	SUB	77
6	9	11
7	a	13
8	IFG	43
9	8	10
a	2	02
b	XFR	67
c	3	03
d	GTO	44

Step	Key	Code
-6-0	SUB	77
1	9	11
2	a	13
3	IFG	43
4	8	10
5	2	02
6	XFR	67
7	2	02
8	GTO	44
9	SUB	77
a	9	11
b	a	13
c	IFG	43
d	8	10
-7-0	2	02
1	XFR	67
2	1	01
3	GTO	44
4	SUB	77
5	9	11
6	a	13
7	IFG	43
8	8	10
9	2	02
a	XFR	67
b	0	00
c	GTO	44
d	SUB	77

Step	Key	Code
-8-0	9	11
1	a	13
2	f	15
3	UP	27
4	e	12
5	x	36
6	b	14
7	DIV	35
8	c	16
9	XEY	30
a	-	34
b	f	15
c	UP	27
d	x	36
-9-0	b	14
1	DIV	35
2	d	17
3	XEY	30
4	-	34
5	DN	25
6	DIV	35
7	YE	24
8	b	14
9	RTN	77
a	UP	27
b	UP	27
c	EEX	26
d	3	03

Step	Key	Code
-a-0	DIV	35
1	DN	25
2	INT	64
3	UP	27
4	EEX	26
5	3	03
6	x	36
7	DN	25
8	-	34
9	UP	27
a	EEX	26
b	7	07
c	DIV	35
d	a	13
-b-0	RUP	22
1	LN	65
2	XEY	30
3	DIV	35
4	DN	25
5	EXP	74
6	UP	27
7	1	01
8	-	34
9	DN	25
a	LN	65
b	XEY	30
c	LN	65
d	AC+	60

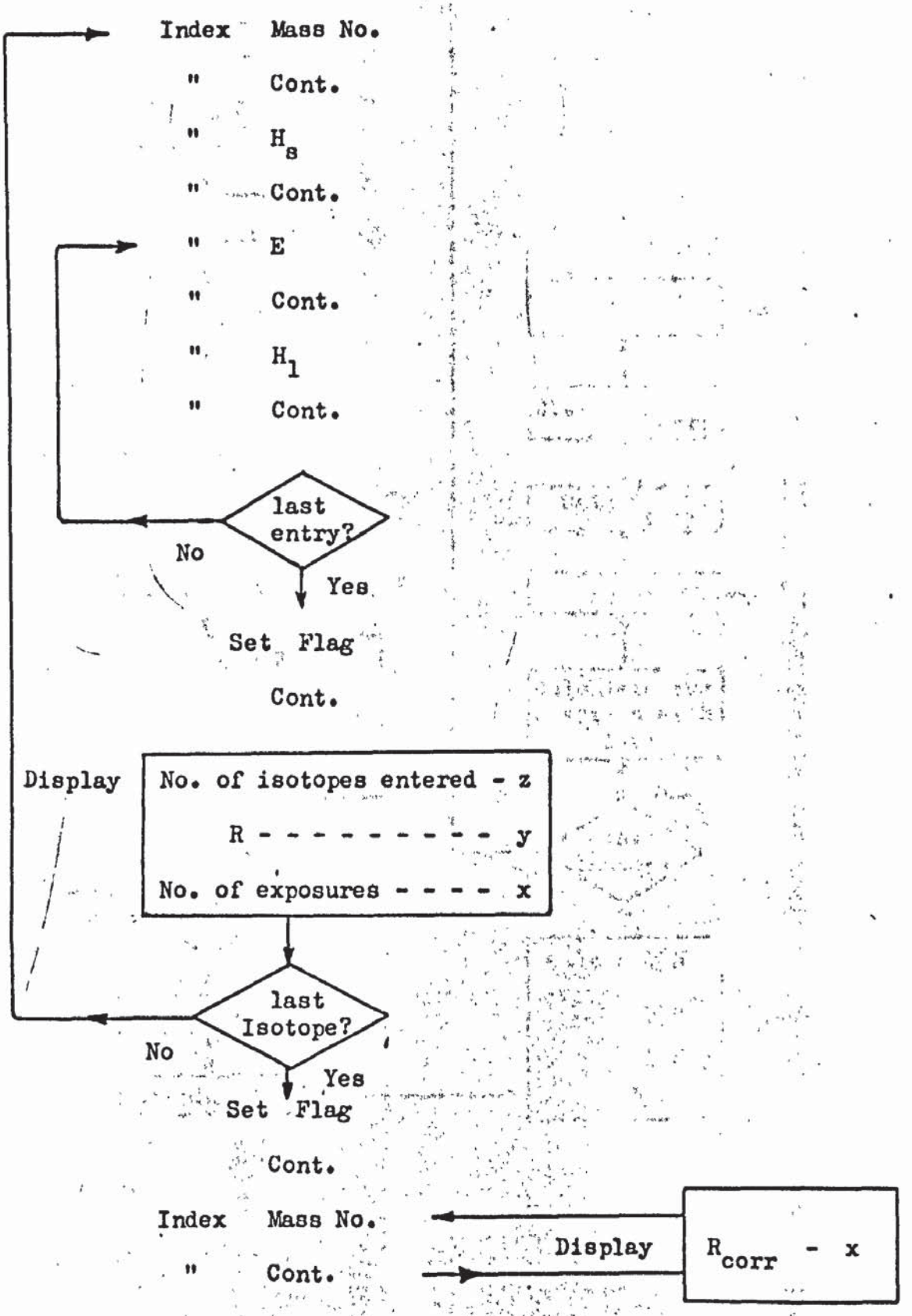
Step	Key	Code
-c-0	UP	27
1	x	36
2	XEY	30
3	YE	24
4	d	17
5	+	33
6	YE	24
7	d	17
8	DN	25
9	x	36
a	c	16
b	+	33
c	YTO	40
d	c	16
-d-0	1	01
1	UP	27
2	b	14
3	+	33
4	YTO	40
5	b	14
6	XFR	67
7	-	34
8	f	15
9	X=Y	50
a	SFL	54
b	CNT	47
c	RTN	77
d	END	46

APPENDIX. 4

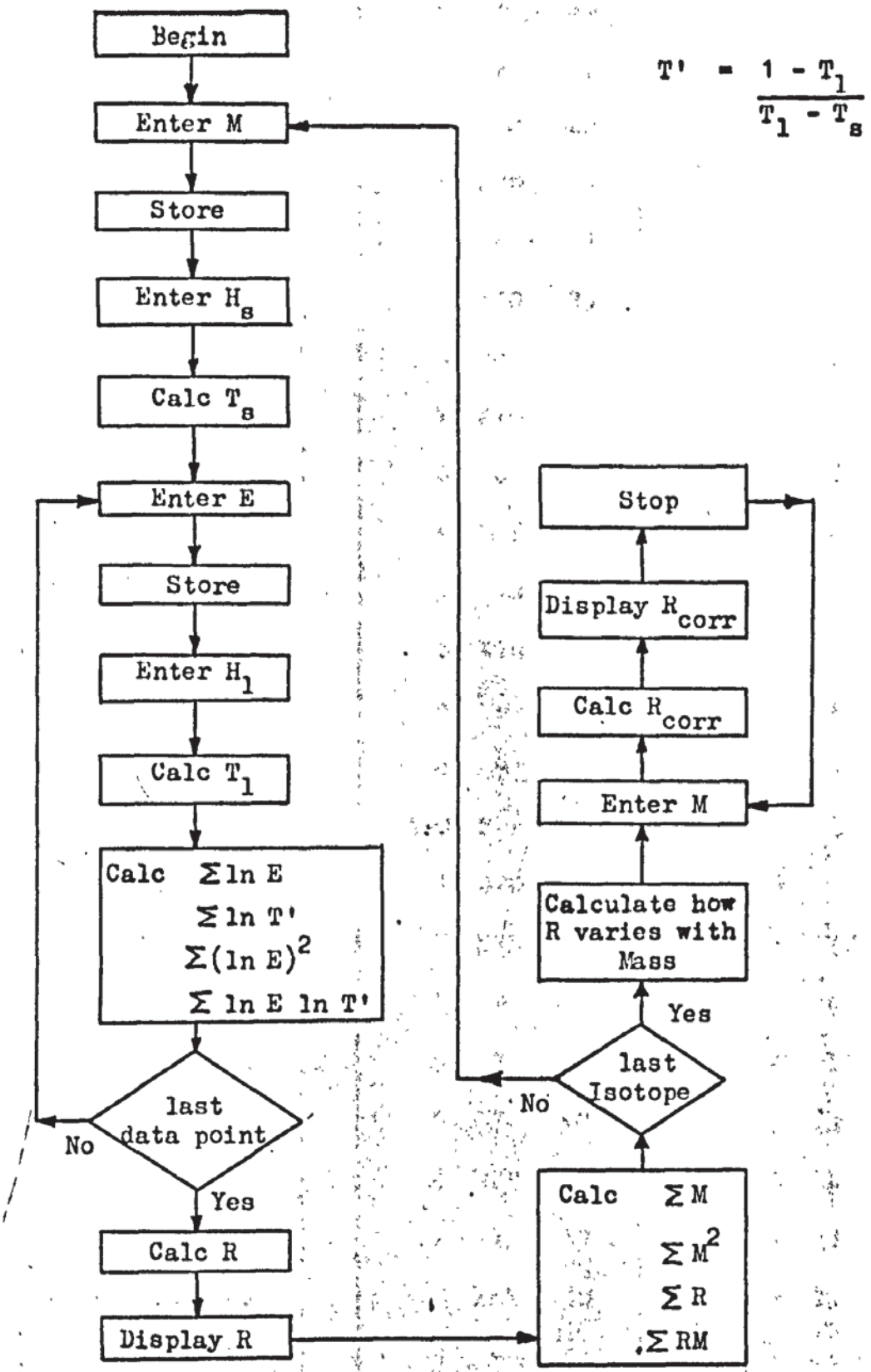
Computer programmes, for Hewlett-Packard 9100B, for the Mathematical Evaluation of Photoplates using the Hull equation

(a) Calculation of R and $R_{corr.}$

Instructions



Flow Chart showing essential steps in the calculation of R



Step	Key	Code
0-0	XTO	23
1	a	13
2	CLR	20
3	XTO	23
4	-	34
5	f	15
6	XTO	23
7	-	34
8	e	12
9	XTO	23
a	-	34
b	d	17
c	XTO	23
d	-	34
1-0	c	16
1	XTO	23
2	-	34
3	b	14
4	a	13
5	XTO	23
6	a	13
7	STP	41
8	GTO	44
9	SUB	77
a	-	34
b	7	07
c	7	07
d	XTO	23

Step	Key	Code
2-0	-	34
1	a	13
2	CLR	20
3	XTO	23
4	b	14
5	XTO	23
6	c	16
7	XTO	23
8	d	17
9	STP	41
a	LN	65
b	XTO	23
c	-	34
d	9	11
3-0	STP	41
1	GTO	44
2	SUB	77
3	-	34
4	7	07
5	7	07
6	UP	27
7	1	01
8	XEY	30
9	-	34
a	UP	27
b	XFR	67
c	-	34
d	a	13

Step	Key	Code
4-0	-	34
1	DN	25
2	DIV	35
3	DN	25
4	LN	65
5	UP	27
6	XFR	67
7	-	34
8	9	11
9	AC+	60
a	UP	27
b	x	36
c	XEY	30
d	YE	24
5-0	d	17
1	+	33
2	YE	24
3	d	17
4	DN	25
5	x	36
6	c	16
7	+	33
8	YTO	40
9	c	16
a	1	01
b	UP	27
c	b	14
d	+	33

Step	Key	Code
6-0	YTO	40
1	b	14
2	STP	41
3	IFG	43
4	6	06
5	9	11
6	GTO	44
7	2	02
8	a	13
9	f	15
a	UP	27
b	e	12
c	x	36
d	b	14
7-0	DIV	35
1	c	16
2	XEY	30
3	-	34
4	f	15
5	UP	27
6	x	36
7	b	14
8	DIV	35
9	d	17
a	XEY	30
b	-	34
c	DN	25
d	DIV	35

Step	Key	Code
8-0	YTO	40
1	c	16
2	XFR	67
3	-	34
4	e	12
5	+	33
6	YTO	40
7	-	34
8	e	12
9	a	13
a	YE	24
b	-	34
c	f	15
d	+	33
9-0	YE	24
1	-	34
2	f	15
3	UP	27
4	x	36
5	XFR	67
6	-	34
7	d	17
8	+	33
9	CNT	47
a	GTO	44
b	-	34
c	0	00
d	0	00

Step	Key	Code
-0-0	YTO	40
1	-	34
2	d	17
3	a	13
4	UP	27
5	c	16
6	x	36
7	XFR	67
8	-	34
9	c	16
a	+	33
b	YTO	40
c	-	34
d	c	16
-1-0	1	01
1	UP	27
2	XFR	67
3	-	34
4	b	14
5	+	33
6	YTO	40
7	-	34
8	b	14
9	c	16
a	UP	27
b	b	14
c	STP	41
d	IFG	43

Step	Key	Code
-2-0	2	02
1	6	06
2	GTO	44
3	+	33
4	1	01
5	5	05
6	XFR	67
7	-	34
8	f	15
9	UP	27
a	XFR	67
b	-	34
c	e	12
d	x	36
-3-0	XFR	67
1	-	34
2	b	14
3	DIV	35
4	XFR	67
5	-	34
6	c	16
7	XEY	30
8	-	34
9	XFR	67
a	-	34
b	f	15
c	UP	27
d	x	36

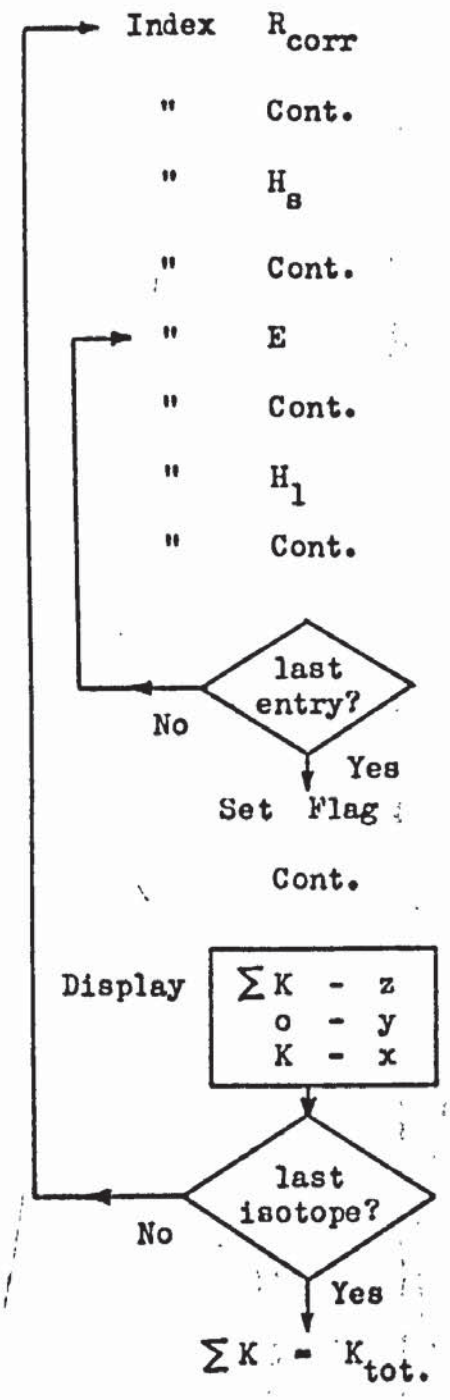
Step	Key	Code
-4-0	XFR	67
1	-	34
2	b	14
3	DIV	35
4	XFR	67
5	-	34
6	d	17
7	XEY	30
8	-	34
9	DN	25
a	DIV	35
b	XFR	67
c	-	34
d	f	15
-5-0	YTO	40
1	b	14
2	UP	27
3	XFR	67
4	-	34
5	b	14
6	DIV	35
7	DN	25
8	x	36
9	XFR	67
a	-	34
b	e	12
c	UP	27
d	XFR	67

Step	Key	Code
-6-0	-	34
1	b	14
2	DIV	35
3	DN	25
4	XEY	30
5	-	34
6	b	14
7	UP	27
8	STP	41
9	XEY	30
a	x	36
b	RDN	31
c	XEY	30
d	+	33
-7-0	RDN	31
1	STP	41
2	GTO	44
3	6	06
4	9	11
5		
6		
7	UP	27
8	8	10
9	8	10
a	•	21
b	3	03
c	0	00
d	DIV	35

Step	Key	Code
-8-0	1	01
1	EXP	74
2	LOG	75
3	DIV	35
4	DN	25
5	EXP	74
6	UP	27
7	1	01
8	XEY	30
9	DIV	35
a	DN	25
b	RTN	77
c	END	46
d		

(b) Calculation of K and K_{tot}.

Instructions



Step	Key	Code
0-0	XTO	23
1	d	17
2	CLR	20
3	XTO	23
4	b	14
5	d	17
6	XTO	23
7	d	17
8	STP	41
9	GTO	44
a	SUB	77
b	6	06
c	0	00
d	XTO	23
1-0	C	16
1	CLR	20
2	1	01
3	XTO	23
4	f	15
5	STP	41
6	XTO	23
7	a	13
8	STP	41
9	GTO	44
a	SUB	77
b	6	06
c	0	00
d	UP	27

Step	Key	Code
2-0	1	01
1	XEY	30
2	-	34
3	UP	27
4	C	16
5	-	34
6	DN	25
7	DIV	35
8	DN	25
9	LN	65
a	UP	27
b	d	17
c	DIV	35
d	DN	25
3-0	EXP	74
1	UP	27
2	a	13
3	DIV	35
4	f	15
5	x	36
6	YTO	40
7	f	15
8	e	12
9	UP	27
a	1	01
b	+	33
c	YTO	40
d	e	12

Step	Key	Code
4-0	STP	41
1	INC	43
2	4	04
3	7	07
4	GTO	44
5	1	01
6	6	06
7	f	15
8	LN	65
9	UP	27
a	e	12
b	DIV	35
c	RDN	31
d	EXP	74
5-0	YE	24
1	b	14
2	+	33
3	YTO	40
4	b	14
5	UP	27
6	CLX	37
7	XEY	30
8	STP	41
9	GTO	44
a	0	00
b	6	06
c		
d		

Step	Key	Code
6-0	UP	27
1	8	10
2	8	10
3	.	21
4	3	03
5	0	00
6	DIV	35
7	1	01
8	EXP	74
9	LOG	75
a	DIV	35
b	DN	25
c	EXP	74
d	UP	27
7-0	1	01
1	XEY	30
2	DIV	35
3	DN	25
4	RTN	77
5	END	46
6		
7		
8		
9		
a		
b		
c		

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